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PROCEEDINGS OF THE SOCIETY OF ARTS.

THIRTY-FOURTH YEAR, 1895-96.

THURSDAY, October 10, 1895.

THE 475th meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., President Walker in the chair.

The minutes of the last meeting were read and approved. Mr. Blodgett presented a report from the Executive Committee announcing the resignation of Mr. C. W. Andrews from the position of Secretary and nominating Dr. Robert P. Bigelow for that office. Dr. Bigelow was duly elected Secretary.

Professor W. T. Sedgwick then read a paper on "What the Institute of Technology Has Done and Is Doing for the Public Health."

This was followed by a general discussion, at the close of which the President thanked Professor Sedgwick for his interesting paper and the Society adjourned.

THURSDAY, October 24, 1895.

The 476th meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., President Walker in the chair.

The minutes of the last meeting were read and approved.

The following papers were read by title:

"Experiments on the Relation of Hysteresis to Temperature," by F. A. Laws and H. E. Warren.

"Studies on the Voltaic Cell (II)," by H. M. Goodwin.

"Synthesis of Diphenylbiphenyl and its Identification as Benzerythrene," by A. A. Noyes and R. M. Ellis.

"Tests from the Engineering Laboratory (III)."

"Occurrence of Trimethylene Glycol as a By-Product in Glycerine Manufacture," by A. A. Noyes and W. H. Watkins.

"Rate of Hydrolysis of Salicine with Acids," by A. A. Noyes and W. T. Hall.

Professor Francis W. Chandler then read a paper on "Early Roman Construction." The paper was illustrated with the lantern. The Society then adjourned.

THURSDAY, November 14, 1895.

The 477th meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., Dr. Francis H. Williams in the chair.

The minutes of the last meeting were read and approved. Messrs. P. H. Dudley, of New York, F. H. Shephard, of Baltimore, Elwyn P. Smith, Webster Wells, Daniel D. Jackson, and Samuel C. Prescott, of Boston, were duly elected Associate Members of the Society.

The following papers were presented by title:

"On Pyrometry," by S. W. Holman.

"On Calorimetry. Methods of Correction for Cooling," by S. W. Holman.

"Thermo-Electric Interpolation Formulæ," by S. W. Holman.

"On Melting Points of Aluminum, Silver, Gold, Copper, and Platinum," by S. W. Holman, R. R. Lawrence, and L. Barr.

Professor Charles Sedgwick Minot, of Harvard University, was then introduced, and read a paper on "The Problem of Embryo-Mechanics." This was followed by a discussion, after which the Society adjourned.

THURSDAY, December 12, 1895.

The 478th meeting of the SOCIETY OF ARTS was held this day at 8 P.M., President Walker in the chair.

The record of the last meeting was read and approved. Messrs. Charles L. Parmelee, of Toledo, and Frank T. Tandy, of Newton, were duly elected Associate Members of the Society.

Mr. Howard A. Carson read a paper on "Various Inventions and Devices for Tunneling and Building Passageways under Rivers and Other Bodies of Water." The paper was illustrated with the lantern. The President extended the thanks of the Society to the speaker for his very interesting paper, and then the Society adjourned.

ROBERT P. BIGELOW, *Secretary.*

CALORIMETRY. METHODS OF CORRECTION FOR COOLING.[1]

By SILAS W. HOLMAN, S.B.

THE following General Method of treating the cooling correction is applicable to nearly all non-continuous calorimetric processes, such as the measurement of specific heats by the "method of mixture," of heat of combustion by the Berthelot or Mahler bomb, etc. It is reliable in ordinary practice within the limits of error imposed by the thermometry and by irregularity of conditions as to surroundings.

Following the brief statement of the "General Method" is that of a "Special Case" of that method, and of a "Modified Method." These are supplemented by a demonstration of the "Theory of the Methods" and a "Critique."

The procedure in the modified method is supposed to be new. Beyond that fact this paper claims the attention merely of those who desire a concise working statement of a method of cooling correction which has stood the test of practice.

GENERAL METHOD. *Procedure.* — Start with the water of the calorimeter at any convenient temperature, *e. g.*, about that of air. If there is a water-jacket around the calorimeter, let it be stirred thoroughly once for all, or, better, continuously. Record its temperature at the beginning and end of the measurement as a possibly useful check.

Let the water of the calorimeter be stirred thoroughly, continuously, and at a uniform rate. Record times and temperatures of the calorimeter each half minute until the completion of the measurements (quarter-minute readings are sometimes preferable). After five or more minutes, at a noted time, drop in the hot substance, or start the calorimetric operation, whatever it may be, continuing the temperature reading throughout the operation, and for at least five (better ten) minutes after its completion. The plot shows a typical set of observations.

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[1] Presented to the American Academy of Arts and Sciences November 13, 1895.

A few readings may unavoidably be missed where there is but one operator, viz., at the time B and in the steep part of BC; but these are unimportant, since the former can be obtained by prolonging the

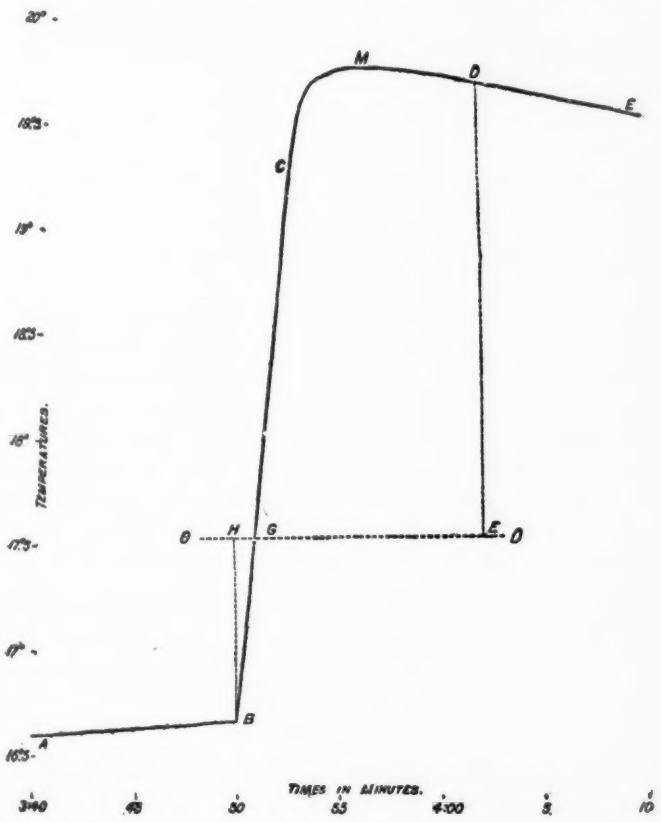


FIG. 1.

line through the data preceding the omission, and the lost part of BC can be drawn in by judgment accurately enough because of the fact that it is of so short duration and must be nearly straight.

The Correction. — The significance of the terms given in this summary will appear on reading the "Theory of the Methods." From a plot, or from the data direct, find the initial rate r_1 and the temperature t_1 at the time m_1; also the final rate r_2 and temperature t_2 at m_2.

From the plot or data compute the mean calorimeter temperature for the time interval $m_2 - m_1$ by the expression

$$T = \frac{1}{n-1}\left[\frac{1}{2}t_1 + b + c + \ldots + \frac{1}{2}t_2\right].$$

Where n is the number of half-minute temperature readings t_1, b, c, . . . , t_2, compute also

$$a = \frac{r_1 - r_2}{t_2 - t_1}, \text{ and } \theta = \frac{r_2}{a} + t_2 \text{ or } = \frac{r_1}{a} + t_1.$$

Then the corrected rise of temperature in the calorimeter will be

$$t_2 - t_1 + a\,(T - \theta)\,(m_2 - m_1),$$

or, if the area method is employed, $t_2 - t_1 + a\,A$.

Special Case. — Where $B\,C$ is sensibly straight and $C\,D$ is of short duration relatively to $B\,C$, then t is to be found by prolonging $E\,D$ to its intersection in I with the vertical through C, the point where the operation ceased or where $B\,C$ begins to deflect from a straight line. From C onward the exchange has been at the rate of $D\,E$, hence the ordinate of I may be taken as the temperature which would have been indicated had all the remaining heat been distributed throughout the calorimeter instantly when the operation ceased. This may be called t_2.

The gain by exchange during the passage from B to C is obviously about $\frac{1}{2}(r_1 + r_2)(m_2 - m_1)$ where m_2 is the time corresponding to t_2. The corrected rise of temperature is then

$$t_2 - t_1 - \frac{1}{2}(r_1 + r_2)\,(m_2 - m_1).$$

Whether this special method is close enough can be determined for any series of measurements by solving a typical example by both it and the general method.

Modified Method. *Procedure.* — By computation from approximate or estimated values of the quantities involved, or from a preliminary trial, determine nearly what the rise of temperature in the calorimeter is to be, and call this Δt. Start with the water of the jacket at, or a degree or two above, the temperature of the air of the room. In the calorimeter, start with the water $\Delta t°$ *below that of the jacket*, or enough more than Δt to allow for unavoidable rise during preliminary manipulations, in short, so that $t°_1$ shall be as nearly as may be

$\Delta t°$ lower than θ. The object of this is to have t_2 so nearly θ that r_2 shall be nearly zero. On the plot of observations (Figure 1) this would cause $A\,B$ to incline upward and $D\,E$ to become nearly hori-

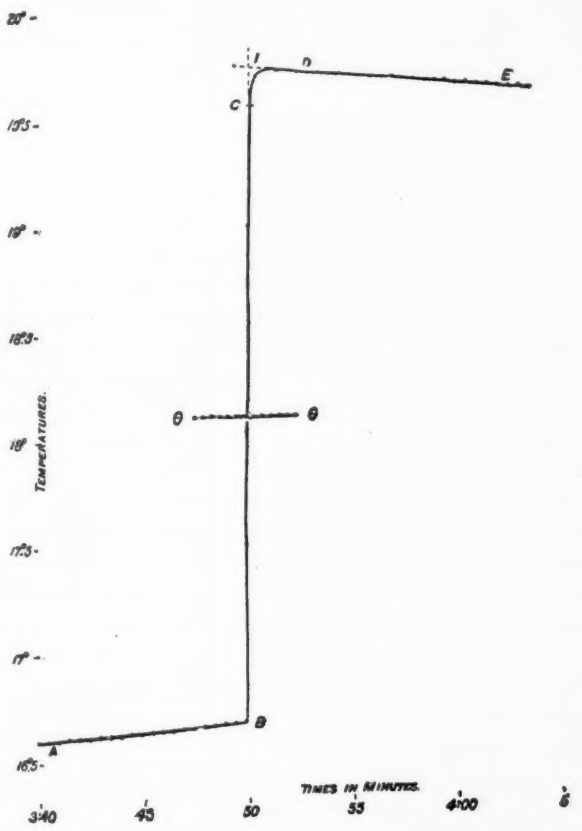


FIG. 2.

zontal. Then proceed precisely as in the general method both as to manipulation and computation.

THEORY OF THE METHODS. — A typical set of readings, for the general method, corrected for thermometric error, and plotted with times as abscissas and temperatures as ordinates, would lie along a line $A\ B\ C\ D\ E$ (Figure 1). This curve should be convex upward

all the way from C to D, there becoming straight. If any concavity shows itself between the maximum M and E, or if the straight line through the points between D and E cuts the curve anywhere between C and D, then the data should be rejected. For the inference, almost without exception, is that the stirring was insufficient to keep the thermometer down to the average calorimetric temperature. This may be due either to the bulb being badly located, so that it is unavoidably heated to excess, or merely to ineffective stirring. The difficulty should be removed and the observation repeated.

The line consists of four portions, viz.: 1. The preliminary readings A to B. 2. The readings during the operation B to some indeterminate point C. 3. Readings C to D while the calorimeter and contents are becoming equalized in temperature. 4. Final, readings after this equalization has become sensibly completed and the calorimeter and contents are cooling, or heating, by exchange with their surroundings. In many cases, as in specific heat determinations, the second and third parts are one, that is, the operation *is* the equalization of temperature between the calorimeter and the substance introduced into it. In the case of a combustion, and many other operations, these two parts are to be distinguished.

The method is based upon Newton's law of cooling. Test observations have shown that this law holds with sufficient accuracy for both open and closed calorimeters — that is, within the uncertainty attributable to varying conditions of surroundings and to thermometric errors.

From the best representative straight line drawn through the observed points between A and B is deduced the initial rate of exchange r_1 (positive for a rising, negative for a falling temperature), expressed in degrees per minute.

For the data between D and E, *i. e.*, through the observations for the final few minutes, which will lie sensibly along a straight line, is deduced similarly the final rate r_2.

Let t_1 be the temperature at the point B, the beginning of the operation. Call this the initial temperature. Then r_1 is the exchange rate at t_1. Let m_1 be the corresponding time. Let t_2 be the temperature at the earliest minute, or half minute, *e. g.*, the point D, at which the line has become straight, *i. e.*, at which the fourth stage has been sensibly attained. Call this the final temperature of the calorimeter, and m_2 the corresponding time in minutes. Then r_2 will be the rate at t_2.

The average temperature of the calorimeter between m_1 and m_2 is next found as follows: Drawing through the points the best representative line $B\,C\,M\,D$, read off its ordinates at each half minute (better each quarter minute) from m_1 to m_2. Instead of a plot the corrected data may be used directly. Call these temperatures $a\ (=t_1)\ b, c, d, \ldots, n\ (=t_2)$ then the average temperature will be

$$T = \frac{1}{n-1}\left[\frac{a}{2} + b + c + \ldots + \frac{n}{2}\right]$$

$$= \frac{1}{n-1}\left[\frac{1}{2}\,t_1 + b + c + \ldots + \frac{1}{2}\,t_2\right].$$

This is, of course, the well-known process. [A slightly better one is to read off the temperature at the end of the first *quarter* minute after m_1 then at intervals of a *half* minute (viz., at $\frac{3}{4}$, $\frac{5}{4}$, etc.) up to m_2 which must therefore be selected at a point an even number of quarter minutes from m_1, as there must be a quarter minute interval at each end. The average of these also gives T.]

By Newton's law of cooling, the rate of gain or loss of heat by a body through exchange with surroundings is directly proportional to the difference of temperature between the body and the surroundings. In calorimetry, provided that the heat capacity of the calorimeter and contents is not changed materially during the process (by the insertion or removal of substances), the rate of gain of temperature through exchange is proportional to the rate of gain of heat, so that the cooling correction may be applied directly to the temperature instead of to the heat.

Under this condition, then, the rate of exchange of temperature when the calorimeter is at any temperature t will be

$$r = a\,(t - \theta)$$

where θ = some constant temperature (representing that of the surroundings which may not be uniform or known) and a = the rate per degree difference between θ and t.

The two quantities a and θ are unknown, but obviously can be computed from the two pairs of observed values r_1, t_1, and r_2, t_2.

For

$$r_1 = a\,(\theta - t_1), \quad r_2 = a\,(\theta - t_2)$$

$$a = \frac{r_1 - r_2}{t_1 - t_2}$$

$$\theta = \frac{r_2}{a} + t_2, \text{ or } \frac{r_1}{a} + t_1.$$

Both a and θ are next computed numerically from the data. θ is best found from the smaller value of t_1, for the reason that it influences the result most largely through its subsequent combination with values near that one.

The gain of temperature by exchange, then, in any short interval of time Δ during which the temperature is t will be $a\ (\theta - t)\ \Delta$. The rate of gain of temperature is $a\ (\theta - t)$, or $a\ \theta - a\ t$, so that, as θ is constant, r varies directly as t. Hence the average rate will be proportional to the average value of t, that is, to T, and will be $a\ \theta - a\ T$, or $a\ (\theta - T)$. The total gain will, therefore, be this quantity multiplied by the duration $(m_2 - m_1)$ of this average rate, or $a\ (\theta - T)\ (m_2 - m_1)$, and the exchange (or "cooling") correction will be this with reversed sign, viz., $-\ a\ (\theta - T)\ (m_2 - m_1)$, or

$$a\ (T - \theta\ m_0 - m_1).$$

The corrected rise of temperature of the calorimeter will then be

$$t_0 - t_0 + a\ (T - \theta)\ (m_0 - m_0).$$

Obviously $(T - \theta)\ (m_2 - m_1)$ is the area $H\,C\,O\,F\,H$ minus the area $B\,G\,H\,B$. This difference, A (in proper units), may, therefore, be measured on a plot by the planimeter or otherwise, and the corrected temperature rise will then be $t_2 - t_1 + a\,A$.

Critique of the Methods. — Three assumptions beyond that of Newton's law of cooling are involved in the employment of these methods, unless otherwise provided for in the computations into which the corrected rise of temperature is introduced: First, that the thermometer indicates the surface temperature of the calorimeter. Second, that the temperature distribution throughout the entire contents of the calorimeter is uniform both when r_1 and r_2 are taken, so that these are really rates of exchange with surroundings, and not resultants in which the desired rate is more or less modified by redistribution within the calorimeter. Third, that the heat capacity of calorimeter and contents is the same both when r_1 and r_2 are taken.

Proper location of thermometer, efficient stirring, and the prevention of direct contact with the calorimeter of any hot or cold object within it readily insure the fulfillment of the first with sufficient closeness.

Wherever the temperature of the calorimeter is varying, uniform distribution of temperature throughout its contents is obviously im-

possible if these are heterogeneous, especially where there is a large metallic mass surrounded by the water, as the bomb in the Berthelot or Mahler combustion apparatus. Such objects will necessarily lag more or less behind the water as the temperature of the latter falls or rises by external exchange. The effect of this is to falsify the apparent rate r_1 or r_2, and still further to vitiate the results through the usual assumption that all parts are at the same temperature. A form of cooling correction taking this into account, and applying to a certain class of cases, has been described by Professor Rowland; but the only method which could entirely eliminate the error would be to arrange the calorimetric process so that the rate of exchange should be sensibly zero or constant during the entire measurement. This means that the jacket temperature must be so controlled as to be always at the temperature of the calorimeter, or at a constant difference from it. While this at first sight appears wholly impracticable, and is so for most cases, I am disposed to think that it might be feasible and helpful in certain investigations, such as the study of the specific heat of water and the mechanical equivalent of heat, using electrical methods of heating, combined with thermoelectric means of detecting and controlling the temperature difference between the calorimeter and jacket.

The "modified method" described above deals with this error in another way. It makes the final rate r_2 as nearly as possible zero, and hence secures the greatest possible constancy of temperature during the portion $C\,D\,E$ of the curve when the rate is about r_2. The advantages gained are as follows: The apparent rate r_2 is sensibly the true rate, since it will in general be much less than the rate of redistribution of heat amongst the contents of the calorimeter. This is of vital importance to freedom from constant or systematic error, because the duration of the rate r_2 is inevitably greater, often much greater, than of any other rate. If, as in the usual process, therefore, it is a large (often the largest) and the least accurately known rate; it is obviously productive of the most serious part of the error of the cooling correction. The Modified Method does not increase the lapse of time preceding the arrival of the final steady condition D, which must in all methods directly or indirectly be the basis from which to deduce t_2. On the other hand, it does increase the percentage reliability of r_2, and by reducing its amount also diminishes the total amount of the correction, thus in a twofold way improving the result. The gain for operations of such a nature that the duration of $C\,D$ is several or

many times that of $B\,C$ is large, being approximately in proportion to those durations. Into that category would fall many of the ordinary calorimetric processes, all those resembling the measurement of specific heats of liquids which cannot be mixed with that of the calorimeter, the use of the bomb for heats of combustion, and almost all processes involving the presence of considerable metallic or glass apparatus within the calorimeter. The method is of much less advantage where the duration of $C\,D$ is brief.

In certain cases there is a slight offsetting increase of error in r_1, namely, when the contents are heterogeneous when both r_1 and r_2 are taken. This occurs in the case of the bomb, but not that of the specific heats of liquids or solids. For then r_1 is a larger rate, and is inaccurate from the cause under consideration. Inasmuch, however, as this rate has during the operation $B\,C$ only a relatively short existence, and as its error as affecting the value of a is divided by $(t_2 - t_1)$, the error introduced by it is small.

It should be noted that if the calorimeter is used as a secondary apparatus, not as a primary or absolute one, the systematic part of many of the errors is further reduced. Thus, for instance, in using the bomb the heat capacity of bomb, calorimeter, and entire contents may best be ascertained by burning in it a known mass of some pure substance of well-determined heat of combustion (*e. g.*, naphthalin), and computing backward from that heat to find the total capacity. This makes the apparatus a secondary one, dependent upon the assumed heat of combustion; but the result is much more reliable than the capacity computed from the assumed or measured specific heats and the masses of the component parts, or measured by the addition of warm water in the well-known manner.

Departure from the third assumption above named cannot be discussed in detail, since the effect varies widely with the change of volume and exposed surface as well as of heat capacity of the contents of the calorimeter in each case. Whether the change of capacity is sufficient to demand allowance can be usually determined by inspection of the case, and a special method of treatment provided. The usual effect is to make the apparent value of r_2 smaller relatively to r_1 than would correspond to Newton's law.

ROGERS LABORATORY OF PHYSICS,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
Boston, May, 1895.

THERMO-ELECTRIC INTERPOLATION FORMULÆ.[1]

By SILAS W. HOLMAN, S.B.

In this paper are collected the several well-known types of formulæ for expressing the thermal electro-motive force of a couple as a function of the temperature of its junctions. Two new formulæ are also proposed. All then are tested against the most reliable, experimental data upon the subject, and their relative merits discussed.

The Existing Formulæ.

Consider a simple closed electric circuit composed of two different metals, each homogeneous in matter and temper, the metals being in contact at two points. For simplicity assume the metals to be in the form of wires joined at their ends. Let one junction be at a temperature of $h°$, the other of $c°$ on the ordinary centigrade scale. Let $\Sigma_c^h e$ be employed as a suggestive symbol to denote the resultant electro-motive force in the circuit, induction being excluded from consideration. Then $\Sigma_c^h e$ is a function of h and c which involves constants dependent upon the nature of the metals, and which may be represented by

$$\Sigma_c^h e = f(h, c).$$

The discovery of the natural expression for $f(h, c)$ is not only of scientific importance, but is urgently needed in the development of the art of pyrometry. At present even a satisfactory empirical formula for interpolation is lacking, the best still being probably that of Avenarius and Tait.

The existing formulæ are the five following:

Ordinary or parabolic.

$$\Sigma_o^t e = at + bt^2 + ct^3 + \ldots \ldots \quad 1.$$

This is, of course, merely a series in ascending powers of t, where one junction is at any temperature $t°$ C., and the other at 0° C., a, b,

[1] Presented to the American Academy of Arts and Sciences, November 13, 1895.

and c being constants. A more general form for the case where the cold junction is at any constant temperature $t_1°$ is

$$\Sigma_{t_1}^{t} e = a\,(t - t_1) + b\,(t^2 - t_1^2) + c\,(t^3 - t_2^3) + \ldots$$

These expressions may, of course, be inverted, giving t as a function of Σe.

Avenarius.

$$\Sigma_c^h e = (h - c)\,\{a + b\,(h + c)\} \quad \ldots \ldots \quad 2.$$

in accordance with the foregoing notation.

Thomson.

$$\Sigma_c^h e = a\,(\tau_h - \tau_c)\left\{\tau_n - \frac{\tau_h + \tau_c}{2}\right\} \quad \ldots \ldots \quad 3,$$

where τ is the absolute temperature, τ_n being that of the "neutral point."

Tait.

$$\Sigma_c^h e = (k' - k)\,(\tau_h - \tau_c)\left\{\tau_n - \frac{\tau_h + \tau_c}{2}\right\} \quad \ldots \ldots \quad 4.$$

Both of the last two reduce to the Avenarius form by the substitution of $t + 273$ for τ.

Barus.

$$e_h + e_c = 10^{P + Qh} + 10^{P' + Q'c} \quad \ldots \ldots \quad 5,$$

where e_h represents the thermal emf. of the hot junction, and e_c that of the cold junction. In view, however, of the existence of the Thomson effect, these symbols can strictly be interpreted only as having the meaning that $e_h - e_c = \Sigma_c^h e$.

NOTE. — With regard to the Avenarius, Thomson, and Tait expressions, it may be remarked that they are not only mutually equivalent, but that if t_c or τ_c becomes 0° C. they reduce at once to the ordinary parabolic form of two terms, $\Sigma_0^t = a_t + bt^2$.

They are all, therefore, forms which must apply if the latter purely empirical expression for the same temperature ranges applies, and with the same closeness, so that it is unnecessary to test more than one of the first four expressions against any one set of data. Also the fact that the Avenarius and Tait equations approximately conform to the observed data does not necessarily in any material degree

strengthen the hypotheses which are adduced to show that these equations are a natural expression of the law.

Without attempting here a further analysis of the components making up the resultant emf., $\Sigma_c^h e$, which is the measured emf. of the thermo-couple, the proposed interpolation formulæ will be merely developed and applied. It may, however, be suggested in passing that there seems to the writer to be little hope of arriving at a close approximation to the natural law except through an expression which shall contain separate terms representing the temperature function of the component arising at the contact of the dissimilar metals and that arising from the inequality of temperature of the ends of each (homogeneous) element (Thomson emf.). The parabolic and Avenarius formulæ would comply in part with this requirement, on the supposition that the emf. at contact varied as the first power, and the Thomson emf. in both wires as the square of the temperature. And looked at from that point of view the neutral point would seem to have an explanation materially different from that usually accorded to it.

The Proposed Formulæ.

Exponential Equation. — The significance of this proposed expression may be thus stated: Suppose the cold junction of the couple be maintained at the absolute zero of temperature, $\tau = 0°$, and its emf. to be consequently zero. Let the other (hot) junction be at any temperature τ_h° absolute. The proposed equation is based on the assumption that the total emf. of the couple would then be representable by

$$e' = m\tau_h^n,$$

where m and n are numerical constants. If then the cold junction were raised to any temperature τ_c there would be introduced an opposing emf. e, which would be expressible by

$$e'' = m\tau_c^n.$$

The resultant emf., $\Sigma_c^h e$, would then be $e' - e''$, and therefore expressible by

$$\Sigma_c^h e = m\tau_h^n - m\tau_c^n \quad . \quad . \quad . \quad . \quad . \quad 6.$$

If in any instance, as is frequently the case in measurements, the temperature of the cold junction is maintained constant while that of the hot junction varies, then $m\tau_c$ becomes a constant, and it will be

convenient to denote this constant by β when $\tau = 273°$ abs. $= 0°$ C. So that for this special case, where the cold junction is at 0° C., and the hot junction at $t°$ C., we have

$$\Sigma_o^t e = m\tau^n - \beta \quad . \quad . \quad . \quad . \quad . \quad 7.$$

This expression is not advanced as a possible natural form of the function $f(h, c)$. It is essentially empirical; is not designed to account separately for the several distinct components entering into Σe, and the fact that it closely fits the experimental data arises chiefly from the well-known adaptability of the exponential equation to represent limited portions of curved lines. The equation also leads to certain inferences which appear inconsistent with the known thermoelectric laws, and fails to explain some known phenomena.

The evaluation of the constants m, n, and β, is, unfortunately, attended by considerable labor. No application of the method of least squares readily presents itself, but by a method of successive approximations the values can be obtained with any desired degree of exactitude. Only two measured pairs of values of $\Sigma_o^t e$ and t are necessary for this approximation method, the third required pair being furnished by $\Sigma_o^0 e = 0$ and $t = 0$; although, of course, by the employment of three pairs of values well distributed in the data a more closely fitting equation might frequently be obtained. The calibration of a thermocouple for pyrometric work can thus be affected by the employment of but two known temperatures; and this, on account of the uncertainty of our knowledge of high melting points, is of importance in high temperature work.

Let $t_o = 0°$ C., t' and t'' be the selected observed temperatures from which to compute the constants, so that $\tau_o = 273°$, $\tau' = t' + 273°$, $\tau'' = t'' + 273°$ abs. And let $\Sigma_o^0 e = 0$, $\Sigma_o^{t'} e$, $\Sigma_o^{t''} e$ be the corresponding observed emfs. of the couple. Then by substituting these in equation 7, and combining the three expressions or their logarithms, we easily deduce

$$\beta = \frac{\Sigma_o^{t'} e}{\left(\frac{\tau'}{\tau_o}\right)^n - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 8.$$

$$n = \frac{\log\left(\Sigma_o^{t'} e + \beta\right) - \log\left(\Sigma_o^{t''} e + \beta\right)}{\log \tau'' - \log \tau'} \quad . \quad . \quad . \quad 9.$$

$$m = \frac{\Sigma_o^{t''} e + \beta}{(\tau'')^n} \quad \text{or} \quad \frac{\Sigma_o^{t'} e + \beta}{(\tau')^n} \quad . \quad . \quad . \quad . \quad 10.$$

By means of these the numerical values of the constants may be calculated from those of τ', τ'', $\Sigma_o^{t'}e$, etc., as follows:

1. Assume as a first approximation some value of n, say $n = 1$, unless some better approximation is in some way suggested. Substituting this value in (8), compute the corresponding value of β.

2. Using this as a first approximation, substitute it in (9), and compute the corresponding value of n.

3. Using this value as a second approximation to n, insert it in (8) and compute a second approximation to β.

4. With this compute a third approximation to n, and so continue until consistent values of β and n are found to the desired number of figures. Then compute m by (10).

The rate of convergence is not rapid, but after one or two approximations have been made an inspection of the rate will enable the computer to estimate values of n which will be nearer than the preceding approximation, and thus hasten the computation.

Where an equation is to be computed to best represent a progressive series of observed values of t and Σe, this method is, of course, open to some objections, since it incorporates in the constants the accidental errors of the selected observations from which the constants are deduced. This difficulty can be sufficiently overcome by computing residuals between the equation and the data, and amending the equation, if necessary, to give them a better distribution.

Logarithmic Formula. — A very simple expression for interpolation is of the general form $\Sigma_o^t e = mt^n$ where m and n are constants. This serves fairly well for a short range $t'' - t'$, when $t' - 0°$ is not less than one third of $t'' - t'$.

The convenience of the expression arises from two facts. First, that its two constants are very easily evaluated either by computation or graphically from the logarithmic expression (whence the name),

$$\log \Sigma_o^t e = n \log t + \log m.$$

Second, that its logarithmic plot is a straight line, since this expression is the equation to a straight line if we regard $\log \Sigma_o^t e$ and $\log t$ as the variables. If, therefore, a series of values of Σe and t are known for a given couple, points obtained by plotting $\log t$ as abscissas and $\log \Sigma e$ as ordinates should lie along a straight line. Thus a couple may be completely "calibrated" for all temperatures by measuring Σe and t for any two values of t (suitably disposed). The constants m and n

may be computed, or a plot of log Σe and log t may be made, and a straight line be drawn through them. Graphical interpolation on this line will then, of course, yield the values of log t, and hence of t, corresponding to observed values of Σe, and *vice versa*, and, if desired, the constants m and n. The expression for t as a function of Σe is, of course,

$$t = m' (\Sigma_o^t e)^{n'}, \text{ or } t = \left(\frac{\Sigma_o^t e}{m}\right)^{\frac{1}{n}}.$$

The formula is well adapted to pyrometric work not of the very highest grade of accuracy, and has been advantageously employed in connection with the LeChatelier thermo-electric pyrometer.[1]

Test of Formulæ.

This will be made by applying the several formulæ to the experimental data of Barus, Holborn and Wien, Chassagny and Abraham, and Noll. These investigators employed modern methods of thermometry and of electrical measur ment. Temperatures are either made in or reduced to the scale of the hydrogen (C. and A.), or of the air thermometer (B., H. and W., N.) Constants for the formulæ will be deduced and the residuals or deviations of the data from the equations (*i. e.*, $\delta =$ data $-$ equation) will be computed for the observed points. For discussion these deviations will be expressed in percentages, viz., $100 \frac{\delta}{e}$, rather than in microvolts or degrees. This is preferable because the process of measurement of the emf., and to some extent, at least, of the temperature, is such as to yield results of a nearly constant fractional or percentage precision at all temperatures rather than of a constant number of microvolts or degrees. Thus by comparing percentages we eliminate a complication arising otherwise from the increasing value of δ as t increases. Incidentally there are also other well recognized advantages frequently attending the comparison of percentages rather than of absolute quantities.

I. *The Barus Data.* — Taking the data in the order of priority, those of Barus will be first employed. The measurements to be used consist of very elaborate and painstaking direct comparisons of several 20 per cent. irido-platinum thermo-couples, with several porcelain-bulb air thermometers, used under the constant pressure method.

[1] Holman, Pyrometry: Calibration of the LeChatelier Thermo-electric Pyrometer, Technology Quarterly, 1895.

Quotations of, or rather interpolations in, his original data[1] are given by Barus[2] later as a basis from which to deduce constants for his proposed equation (*vide ante*):

$$e + e_o = 10^{P+Qt} + 10^{P'+Q't}.$$

Barus' numerical values for the constants are

$e_o = 45\,680$ microvolts.

$P = 4.6515$ $\qquad Q = 1.106 \cdot 10^{-4}$

$P' = 2.849$ $\qquad Q' = -\ 3.01 \cdot 10^{-3}$

These constitute his equation 3, for which e_o corresponds to 20° C. The data and the deviations which I have computed for it, viz., $\delta =$ data — equation, are given in Table I. The last column gives the deviations expressed in percentages, viz., $100\,\frac{\delta}{E}$ where $E = e + e_o + 1880$. This value of E is adopted to make the percentages comparable with those in subsequent discussions. The number 1880 is 1730 + 150, which are the values of e_o and $\Sigma_o^{20} e$ of the next two pages.

TABLE I.

Barus' American Journal of Science Data.

$t°$	$e + e_0$ observed. *mv.*	$e + e_0$ computed from equation 3. *mv.*	δ *mv.*	$100\,\frac{\delta}{E}$ per cent.
0° C.	— 150	....	....	....
100	680	653	+ 27	+ 1.11
200	1,650	1,657	— 7	— 0.20
300	2,760	2,788	— 28	— 0.60
400	3,950	3,994	— 44	— 0.80
600	6,560	6,551	+ 9	+ 0.11
800	9,310	9,273	+ 37	+ 0.34
1,000	12,200	12,140	+ 60	+ 0.43

[1] Barus, C., United States Geological Survey Bulletin, 54, 1889: Philosophical Magazine, xxxiv, 1 (1892).

[2] Barus, C., American Journal of Science, xlviii, 332 (1894). See also xlvii, 366 (1894).

The lines *A B* and *C D* on the plot, Figure 1, constructed with percentage deviations as ordinates and temperatures as abscissas, show clearly that the deviations are systematic. Upon inspection of this plot it appears that the data may be separated into two groups, one including 0°–300°, the other 400°–1,000°, which appear to have entirely distinct forms of systematic error. This division corresponds to two distinct groups of data, one extending from 0° to 300°, the other including the second group, and extending from 350° to 1,075°. The latter were given in the *Bulletin* as the final results of the high temperature comparisons of the irido-platinum couple with porcelain-bulb air thermometers. The detailed statement of the 0° to 300° comparison I have not seen. Although the discrepancy between the two sets of systematic deviations is not extremely large, yet it has seemed to me that it was beyond the limits of concordance in the higher temperature work, and that it would be better for the present purpose to deal solely with the 330° to 1,075° data. Two points regarding Barus' work should be noticed: one, the strikingly high degree of concordance between individual observations even with different thermometer bulbs and different thermo-couples; the other, the remark in which Barus notes a possibility of being able to still further reduce the "stem error" entering into the result, which, so far as I am aware, has not yet been done.

The high temperature air thermometer comparisons (*Bulletin*, Series I, II, III, IV, and V) of Barus are so numerous (108) and so distributed that the labor of utilizing them simply for deducing constants and testing an equation would be excessive. Also, they are too concordant to permit interpolation on a direct plot without a sacrifice of some of their precision. For the purposes of discussion, therefore, I averaged them in nine groups: The first group contained all where the emf. lay between 3,000 and 4,000 microvolts; the second group between 4,000 and 5,000 microvolts, and so on by steps of 1,000 microvolts, except that the seventh group covered 2,000 microvolts, from 9,000 to 11,000. These groups were not exactly equal in number of observations, and therefore in weight, nor is the arithmetical average a strictly legitimate value where the function is not linear; but, as easily seen by inspection of the originals, the errors thus introduced are negligible. In Table II, Columns 1 and 2 give the direct values of the averages. Column 3 reduces $\Sigma^t_{20} e$ to $\Sigma^t_0 e$ by adding 150 microvolts, the value of $\Sigma^o_{20} e$ being elsewhere given by Barus as — 150 microvolts.

TABLE II.

BARUS' AIR THERMOMETER COMPARISONS. SERIES I–V.

			AVENARIUS.		EXPONENTIAL.		LOGARITHMIC.	
t	$\Sigma_0^t e$ mv.	$\Sigma_0^t e$ mv.	δ = data − equation. mv.	Per cent. $= 100\,\frac{\delta}{e}$	δ = data − equation. mv.	Per cent. $= 100\,\frac{\delta}{e}$	δ = data − equation. mv.	Per cent. $= 100\,\frac{\delta}{e}$
0°.C.	(−150)	0	0	0.	+ 23	+ 1.3	....	....
378.5	3 679	3 829	− 84	− 4.0	− 66	− 1.2	− 33	− 0.60
440.3	4 508	4 658	+ 18	+ 0 28	+ 18	+ 0 28	+ 30	+ .47
522.0	5 486	5 636	− 4	− 0.07	− 25	− 0.34	− 36	− .50
588.4	6 404	6 554	+ 70	+ 1.1	+ 33	+ 0.40	+ 9	+ .12
672.1	7 550	7 700	+ 110	+ 1.5	+ 60	+ 0.64	+ 26	+ .28
745.6	8 530	8 680	+ 82	+ 0.92	+ 26	+ 0.25	− 9	− .10
840.1	9 898	10 048	+ 101	+ 1.0	+ 49	+ 0.41	+ 26	+ .22
946.6	11 396	11 546	+ 9	+ 0.07	− 19	− 0.14	− 13	− .10
1 019.7	12 475	12 626	− 45	− 0.32	− 45	− 0.32	− 10	− .07
Average percentage deviations . .				0.93		0.53		0.27

The Avenarius equation applied to these data yields $\Sigma_0^t e = 9.104\,t + 3.249 \cdot 10^{-3}\,t^2$. [Microvolts. Range, 350° to 1,075°C.] Computing from this equation values of $\Sigma_0^t e$ for the successive values of t in Column 1, and subtracting them from the data in Column 3, gives the deviations between data and equation. These are expressed in microvolts in Column 4, and in percentages in Column 5, the percentage being reckoned in terms of e_t as deduced by the exponential formula. Objections may be felt to this use of e_t (here, as throughout the subsequent tables) as a basis, since e_t involves e_o, which is an extrapolated value, certainly not exact, and possibly wide of the truth. Such a criticism is valid, but inasmuch as the values of e_o employed are nearly equal, and as the percentage deviations are used merely for purposes of expressing relative accuracy, the possible error involved is nearly annulled. Hence, although it would be better to compute δt, and express this as a percentage of the absolute temperatue τ, the added labor did not seem justified by the small gain.

The exponential equation applied to the Barus data yields

$$\Sigma_o^t e = 0.7691\tau^{1.373} - 1{,}730,$$

or [Microvolts. Range of data, 350° to 1,075° C.]

$$e_\tau = 0.7691\tau^{1.373}, \text{ and } \beta = 1{,}730\, mv.$$

NOTE. — This equation was deduced with the value 0° C. = 273°.7 absolute, whereas in all subsequent tables 0° C. = 273°.0 absolute is employed as a more probable value. The numerical values of the constants are, therefore, subject to a slight modification, but as for the present purpose we are concerned only with δ, which would not be sensibly changed, the recomputation is not worth while.

Columns 6 and 7, Table II, give δ and its percentage value for the exponential equation.

The Barus equation. — The excessive labor involved in the evaluation of the constants P, Q, P', and Q' of Barus' proposed equation detracts so seriously from its usefulness that I have also allowed it to deter me from computing them for the above tabulated values. The comparison of the values of δ for his equation 3 and for an approximate exponential of my own based on the same data is, however, decidedly in favor of the latter.

The logarithmic equation applied to the Barus data yields

$$\Sigma_o^t e = 2.665\, t^{1.220}, \text{ or its equivalent,}$$

$$\log \Sigma_o^t e = 1.220 \log t + 0.42570.$$

The deviations are given in the last two columns of Table II.

II. *Holborn and Wien data.* — This important comparison [1] of the rhodo-platinum thermo-couple with the porcelain-bulb air thermometer up to high temperatures was performed under the auspices of the Reichsanstalt at Berlin, and appears to be, on the whole, the most important and reliable contribution to this subject in recent years. The experimental work was evidently conducted with great care, and although not showing the concordance of results, nor the multiplication of observations of Barus' work, yet in respect to stem-exposure correction, to the exposure of the thermal junction, and to direct measurement of the coefficient of expansion of the bulb, it is probably more free from systematic error. It is to be regretted that the results were not more thoroughly discussed, and that neither a chemical analysis nor even a statement was given to indicate the reliability

[1] Holborn and Wien, Zeit. f. Instk., xii, 257, 296 (1892). Also in full in Wied. Ann., xlvii, 107 (1892).

of the stated percentage composition of the various alloys used. For when closely examined the data seem to indicate a determinate relation between the composition and the emf., as was shown by a relation discovered between the constants in my exponential equations for the various alloys. The deviations were only such as might be attributed to uncertainty of composition, but as no measure of the latter was given a statement of the relations and interesting inferences from them is not warranted. It is also unfortunate that an analysis, or at least a definite statement of the percentage purity, was not given for the gold, copper, and silver, whose melting points were observed. The assertion that the gold showed on qualitative analysis only a trace ("spur") of copper, and the silver a trace of iron, is hardly definite. The value of the whole work would have been enhanced by these additions far more than in proportion to the comparatively small labor demanded by them, and such completeness is naturally to be counted upon in work emanating from the source of this. It is to be hoped that a continuation of this research is in progress, and that additional high melting points may be measured.

Table III, Columns 1 and 2, quotes the interpolated mean values of several comparisons expressed in "international" microvolts and degrees centigrade. With regard to these data it should be stated that below about 400° they were not supposed to be of as high accuracy as above that point. Also, that, owing to unavoidable circumstances, the data below 300° were obtained with only a single air-thermometer bulb, and similarly those above about 1,300° with one bulb only, but a different one, while the data intermediate between 400° and 1,300° are the mean of observations with the two bulbs. This fact may partially account for the erratic character of the residuals above 1,300°, where the deviations are so great and so distributed (see plot) as to render these observations of very little service. Direct comparison with the air thermometer was made with one 10 per cent. rhodo-platinum couple *A* only.

The parabolic formula applied to these by Holborn and Wien, when corrected as to decimal points,[1] is

$$t = 1.376 \cdot 10^{-1} (\Sigma_o^t e) - 4.841 \cdot 10^{-6} (\Sigma_o^t e)^2 + 1.378 \cdot 10^{-10} (\Sigma_o^t e)^3.$$

[Range, — 80° C. to + 1,445° C.]

The residuals are given in Table III, Columns 3 and 4.

[1] The equation at both references, and stated to be in microvolts and degrees, is erroneously printed as $t = f(e) = 13.76e - 0.004841e^2 + 0.000001378e^3$.

The Avenarius formula applied to the Holborn and Wien data, with constants deduced from $t = 584°$ and 1,273°, becomes

$$\Sigma_o^t e = (t - t_o)\,\{7.2188 + 0.00\,229\,94\,(t + t_o)\},$$

or, [Range, 0° to 1,445° C.]

$$= 7.2188\,t + 2.2994 \cdot 10^{-3}\,t^2.$$

The deviations in microvolts and percentages from this equation are given in Columns 5 and 6, Table III.

The exponential equation fitting these data most closely, and coinciding with them at nearly the same points as the others, viz., at about 584° and 1,250°, is

$$\Sigma_o^t e = 0.57\,674\,\tau^{1.377} - 1\,310,$$

or, [Range, 0° to 1,445° C.]

$$e = 0.57\,674\,\tau^{1.377},\ \beta = 1\,310.$$

The deviations in microvolts and percentages are in Columns 7 and 8, Table III.

The logarithmic equation applied to the Holborn and Wien data yields

$$\Sigma_o^t e = 2.1682\,t^{1.2156},$$

or,

$$\log \Sigma_o^t e = 1.2156 \log t + 0.36\,610.$$

The deviations are given in the last two columns of Table III.

Holborn and Wien not only compared the 10 per cent. rhodo-platinum couple *A* directly with the air thermometer, but compared with *A* seven other couples in which one element was platinum and the other a rhodo-platinum alloy, the percentage of rhodium being stated respectively as for C_1 and C_2, 10 per cent. (These two I have combined under *C*.) *D*, 9 per cent., *E*, 11 per cent., *F*, 20 per cent., *G*, 30 per cent., *H*, 40 per cent. For the present purpose I have combined the data, which were differences of emf. between *C* and *A*, *D* and *A*, etc., with the corresponding emf. of *A*, and thence have deduced the exponential equations for each of the alloys. Table V gives the percentage deviations of these alloys from the exponential equation (data—equation), and Table IV shows the values of m, n, and β for those equations.

TABLE III.

HOLBORN AND WIEN. AIR THERMOMETER COMPARISONS. ALLOY "A."

		H. AND W. EQN.		AVENARIUS.		EXPONENTIAL.		LOGARITHMIC.	
t Centigrade.	$\Sigma^t_o e$.	δ = data-equation.	Per ct. $= 100 \frac{\delta}{e}$	δ = data-equation.	Per ct. $= 100 \frac{\delta}{e}$	δ = data-equation.	Per ct. $= 100 \frac{\delta}{e}$	δ = data-equation.	Per ct. $= 100 \frac{\delta}{e}$
	mv.	*mv.*		*mv.*		*mv.*		*mv.*	
80°	— 361	...	...	...	...	...	...	...	...
0	0	0	0	0	0	0	0	0	0
82	500	— 84	—4.6	—107	—5.1	— 69	—3.6	+ 40	+ 2 2
154	1 000	—147	—6.1	—166	—7.2	—122	—4.8	+ 11	+ 0.50
220	1 500	—135	—5.0	—199	—7.1	—140	—4.7	— 27	— 1.0
273	2 000	—150	—4 5	—142	—4 3	— 85	—2 6	+ 16	+ 0.50
329	2 500	—130	—3 6	—124	—3.3	— 73	—1.9	+ 11	+ 0.30
379	3 000	— 60	—1 4	— 66	—1.5	— 24	—0.57	+ 45	+ 1.0
431	3 500	— 30	—0 60	— 41	—0.9	— 6	— .12	+ 45	+ 0.90
482	4 000	0	0	— 14	— .22	+ 8	+ .15	+ 41	+ .80
533	4 500	+ 10	+ .17	— 1	0	+ 9	+ .15	+ 27	+ .50
584	5 000	0	0	0	0	— 2	— .03	+ 1	+ .01
633	5 500	0	0	+ 9	+ .13	— 4	— .06	— 13	— .20
680	6 000	+ 10	+ .11	+ 23	+ .38	+ 5	+ .07	— 15	— .20
725	6 500	+ 30	+ .40	+ 58	+ .74	+ 26	+ .33	— 1	— .01
774	7 000	— 10	— .12	+ 35	+ .42	— 5	— .06	— 39	— .47
816	7 500	+ 20	+ .22	+ 78	+ .90	+ 33	+ .37	— 8	— .10
862	8 000	0	0	+ 69	+ .74	+ 19	+ .20	— 24	— .26
906	8 500	— 20	— .20	+ 72	+ .74	+ 19	+ .20	— 25	— .25
952	9 000	— 55	— .55	+ 44	+ .43	— 10	— .10	— 53	— .52
996	9 500	— 88	— .80	+ 29	+ .26	— 24	— .22	— 67	— .60
1 038	10 000	— 88	— .80	+ 29	+ .25	— 20	— .18	— 57	— .50
1 089	10 500	—100	— .85	+ 22	+ .20	— 23	— .20	— 54	— .43
1 120	11 000	—100	— .80	+ 31	+ .25	— 7	— .06	— 22	— .19
1 163	11 500	—140	—1.1	— 6	— .05	— 33	— .26	— 51	— .40
1 200	12 000	— 96	— .74	+ 26	+ .20	+ 9	+ .07	+ 2	+ .02
1 241	12 500	— 96	— .70	0	0	— 3	— .03	— 8	— .06
1 273	13 000	0	0	+ 84	+ .60	+ 94	+ .67	+111	+ 0 80
1 311	13 500	+ 36	+ .24	+ 84	+ .57	+110	+ .80	+140	+ 0.90
1 354	14 000	+ 24	+ .17	+ 10	+ .07	+ .58	+ .38	+107	+ 0.70
1 402	14 500	— 60	— .40	—141	— .90	— 65	— .41	+ 2	+ .01
1 445	15 000	— 72	— .45	—231	—1.40	—128	— .80	— 38	— .23
ad. for 0 to 1445.			1 12		1.15		0.77		1.46
ad. for 341 to 1445.			0.39		0.43		0 25		0.38
ad. for 431 to 1241.			0.43		0.36		0.15		0.34

TABLE IV.

Designation of the alloy.	Nominal percentage of rhodium.	Exponential equation constants. m.	n.	β mv.
D	9	1.36 71	1.250	1 517
C	10	0.95 596	1.310	1 485
E	11	0.81 734	1.336	1 469
A	10	0.57 689	1.377	1 305
F	20	0.22 865	1.522	1 167
G	30	0.06 599 0	1.708	956
H	40	0 06 303 4	1.720	977

TABLE V.

HOLBORN AND WIEN. COMPARISON OF ALLOYS.

T.	D.	A.	C.	E.	F.	G.	H.	Average A to H.
0°C.	0	0	0	0	0	0	0	0
154	..	— 4 8	...	—4.0	...	— 5.0	— 4 4	— 4.5
273	—0.9	— 2.6	— 2.7	— 2 2	— 2.3	— 3.5	— 2.3	— 2.6
379	+ 2.1	— 0.57	— 0.80	— 0.50	— 1.3	— 0.60	— 0.25	— 0.67
482	+ 2.6	+ .15	— .03	0	— 0.6	+ .22	+ .46	— 0.03
584	+ 0.90	— .03	+ .19	+ .08	+ .13	+ .30	— .03	+ 0.02
680	— .30	+ .07	+ .13	+ .13	+ .12	— .16	— .26	0.00
774	— .19	— .06	— .08	— .02	— .12	— .42	— .46	— 0.19
862	+ .23	+ .20	+ .20	+ .20	+ .09	+ .15	— .11	+ 0.12
952	+ .20	— .10	0	— .11	— .15	+ .09	— .24	— 0.08
1 038	+ .12	— .18	— .10	— .21	— .27	+ .04	— .14	— 0.16
1 120	— .15	— .06	— .09	— .02	+ .10	+ .01	+ .22	— 0.01
1 200	+ .02	+ .07	0	+ .10	0	+ .04	0	+ 0.03
1 273	....	+ .67	+ .70	+ .80	+ .80	+ .43	+ 1.0	+ 0.73
1 354	....	+ .38	+ .60	+ .67	+ .51	+ .30	+ 1.0	+ 0.58
1 445	....	— .80	— .38	— .50	....	— .90	— 0.40	— .60
a. d. 400°–1,200°	.52	.15	.09	.10	.12	.16	.21	.07
a. d. 400°–1,445°	....	.25	.21	.24	(.24)	.23	.36	
		Direct from Air Th.						

III. *Chassagny and Abraham Data.* — The apparently very careful measurements of these observers cover a range of 0° to 100° C., with observations at 25°, 50°, 75° only. This is too short, and the intervals are too great to render the work of much service in testing a general formula; but if its accuracy is as high as about 0°.01, as it appears to be, this in part offsets the disadvantage. Measurements of $\Sigma_o^t e$ and t were made with four thermo-couples with the results shown in Table VI (international microvolts and degrees centigrade on hydrogen scale).

TABLE VI.

Couple.	$\Sigma_o^{100} e$.	$\Sigma_o^{75} e$.	$\Sigma_o^{50} e$.	$\Sigma_o^{25} e$.
Fe-Cu.	1 093.2	864.9	604.8	315.5
Fe-Pt. Rh. . . .	895.1	708.9	496.1	259.1
Fe-Ag.	1 123.0	885.6	617.4	321.1
Fe-Pt.	1 685.1	1 278.9	859.9	432 1

The Avenarius equation was applied to these data by Chassagny and Abraham[1] in the form $\Sigma_o^t e = at + bt^2$.

They evaluated the constants from the 50° and 100° data. With these they computed the temperatures which the equation would yield by insertion of the observed values $\Sigma_o^{25} e$ and $\Sigma_o^{75} e$. These values are given in Table VII, Columns 2 and 3.

The exponential equation applied to these data for Fe — Pt becomes

$$\Sigma_o^t e = 105.096\, t^{0.7360} - 6\,525.3. \qquad \text{[Range, 0° to 100° C.]}$$

The values of t corresponding to the observed values $\Sigma_o^{25} e$ and $\Sigma_o^{75} e$ are given in Table VII. It has not seemed for the present purpose worth while to make similar computations for the other couples, as they would not materially affect the inferences to be drawn.

The logarithmic equation yields

$$\Sigma_o^t e = 19.2946\, t^{0.97\,059\,5},$$

or,
$$\log \Sigma_o^t e = 0.97\,059\,5 \log t + 1.28\,543\,6.$$

The deviations are given in the table.

[1] Chassagny et Abraham, Ann. de Ch. et de Phys., xxvii, 355 (1892).

TABLE VII.

Couple.	Avenarius. (C. and A.)		Exponential.				Logarithmic.	
	t.	δt.	t.	δt.	δ mv.	$100\frac{\delta}{e}$ Per cent.	δt.	δ mv.
Fe — Cu . . .	24°.88	+ 0°.12	....	....	....	....	....	....
Fe — Pt.Rh. .	24.885	.115	....	....	....	....	....	....
Fe — Ag . . .	24.87	.13	....	....	....	....	....	....
Fe — Pt . . .	24.87	.13	24°.80	+ 0°.20	— 2.6	— 0.037	+ 0°.52	— 6.7
Fe — Cu . . .	75.13	— 0.13	....	....	....	....	....	....
Fe — Pt.Rh. .	75.135	.135	....	....	....	....	....	....
Fe — Ag . . .	75.135	.135	....	....	....	....	....	....
Fe — Pt . . .	75.135	.135	75°.15	— 0°.15	+ 2.5	+ 0.032	— 0°.26	+ 4.3

IV. *The Noll Data.* — A contribution of much permanent value to the data on thermo-electrics has recently been made by Noll,[1] who has measured $\Sigma_0^t e$ and t for thirty-two couples over a range in most cases of 0° C. to 218° C. The metals employed (including carbon) were usually of a high and stated degree of purity, and consisted of eighteen different substances, two of which were alloys (German silver and brass), and the remainder samples of different degrees of purity or hardness of the pure substances. The couples contained as one element, for the most part, either copper or mercury. Temperatures were reduced to the air thermometer scale.

The Avenarius formula was applied to fourteen of the more important of them by Noll.

The exponential equation I have applied to the same data. It has not seemed essential to reproduce here the entire series of data and the deviations of both equations. They are, therefore, presented in a somewhat more digested form. Table VIII gives the constants for the exponential equation (those for the Avenarius may be found in Noll's article), the mean deviations, = data — equation, for each series, and the mean percentage deviations ($= 100\frac{\delta}{e}$). (See remark under

[1] Noll, Wiedermann's Annalen, liii, 874 (1894).

TABLE VIII.

NOLL'S DATA ON PURE METALS.

Couple.	m.	n.	β mv.	Av. Per Cent. Deviations.	
				Avenarius.	Exponential.
Au — Hg . .	$4.6954 \cdot 10^{-3}$	2 136	750.4	± 0 27	± 0.17
Ag — Hg . .	$2.8637 \cdot 10^{-3}$	2.206	677.8	0.33	0.15
Ni — Cu . .	$8.2333 \cdot 10^{-1}$	1.511	3 950.2	0.30	0.17
(Cd — Cu . .	$3.7617 \cdot 10^{-11}$	4.94	40.7	0.48	3.40)
Br — Cu . . .	$2.4969 \cdot 10^{-1}$	1.366	531.1	0.14	0.13
Zn — Hg . .	$8.2890 \cdot 10^{-4}$	2.420	651.6	0.15	0.18
Pb — Cu . .	$1.7674 \cdot 10^{-2}$	1.800	429.0	0 05	0 07
Cu_1 — Hg . .	$4.6726 \cdot 10^{-3}$	2.130	768.4	0.12	0.11
[Fe — Hg . .	$1.0913 \cdot 10^{+2}$	0.7220	6 264.2]	....	....
Co — Hg . .	$8.3295 \cdot 10^{-3}$	2.166	1 575.2	0.26	0.22
Pt_1 — Cu . .	$2.1475 \cdot 10^{-3}$	2.266	711.1	0 08	0.12
Pt_2 — Cu . .	$1.1095 \cdot 10^{-3}$	2.353	599.0	0.19	0.25
Sn_1 — Cu . .	$4.2021 \cdot 10^{-2}$	1.667	482.8	0.21	0.09
Mg — Cu . .	$2\ 0449 \cdot 10^{-2}$	1.782	448.7	0 15	0.17
Al — Cu . . .	$7.5643 \cdot 10^{-2}$	1.590	565.3	0.11	0.12
G. s. — Cu . .	$2.0454 \cdot 10^{-1}$	1.684	2 589.9	0.06	0.05
Average, omitting Cd — Cu and Fe — Hg.				0.17	0.14

"Barus Data.") Table IX groups the percentage deviations under their nearest values of t for exhibiting their systematic character. The fact that the experimental method brought the observations all very nearly to the respective temperatures t given in the table renders this grouping possible. I have taken the liberty of correcting a few obvious numerical errors, and of dropping a very few values evidently containing a mistake.

It may, perhaps, not be out of place here to caution those who would make use of Noll's data to their full accuracy that his original and not his interpolated numbers should be resorted to. The approx-

TABLE IX.

AVENARIUS EQUATION. DATA — EQUATION IN PER CENT.

	15°.	57°.	100°.	138°.	181°.	198°.	217°.
Au — Hg . . .	— .10	— .40	0	+ .05	+ .60	+ .90	0
Ag — Hg . . .	— .13	+ .20	0	+ .21	— .50	— 1.30	0
Ni — Cu . . .	— .26	— .15	0	0	— .22	— .31	— 1.17
Br — Cu . . .	....	— .10	0	+ .20	+ .17	+ .35	0
Zn — Hg . . .	....	— .03	0	+ .09	+ .41	+ .40	0
Pb — Cu . . .	....	— .03	0	— .11	+ .12	— .04	0
Cu_1 — Hg . . .	+ .02	— .16	0	+ .01	+ .15	+ .38	0
Co — Hg . . .	....	....	0	+ .42	0	....	— .56
Pt_1 — Cu . . .	....	— .12	0	— .06	+ .09	+ .21	0
Pt_2 — Cu . . .	....	— .13	0	— .11	0	+ .67	— .21
Sn_1 — Cu . . .	....	— .20	0	0	+ .34	+ .40	+ .30
Mg — Cu . . .	....	+ .11	0	+ .22	— .37	+ .11	0
Al — Cu . . .	....	+ .16	0	+ .18	— .18	+ .15	0
G. s. — Cu . .	....	— .01	0	+ .16	+ .11	....	0
Average . . .	— .12	— .07	0	+ .09	+ .05	+ .16	— .12

imate linear interpolation which he has employed is not as accurate as his experimental data demand.

The logarithmic equation applied to the Cu_1 — Hg couple as typical of the Noll data yields

$$\Sigma_o^t e = 2.57\,434\ t^{1.2250},$$

or

$$\log \Sigma_o^t e = 1.2250 \log t + 0.41\,066\,5.$$

The residuals to this expression are given in Table IX.

DISCUSSION OF THE DEVIATIONS.

Plots are given in diagram, drawn with temperatures as abscissas and percentage deviations between the data and the sundry equations as ordinates (*i. e.*, $100\ \frac{\delta}{e}$, where δ = data — equation). Inspection will show that, with one exception (viz., the logarithmic equation applied to

TABLE IX. — *Continued.*

EXPONENTIAL EQUATION. DATA—EQUATION IN PER CENT.

	15°.	57°.	100°.	138°.	181°.	198°.	217°.
Au — Hg . . .	+ .01	— .12	— .06	— .06	+ .09	+ .12	— .80
Ag — Hg . . .	— .18	+ .22	0	+ .05	— .03	0	— .50
Ni — Cu . . .	— .26	— .16	0	+ .07	0	0	— .72
Br — Cu . . .	....	— .06	— .01	+ .12	+ .20	— .26	— .13
Zn — Hg . . .	....	— .30	+ .02	+ .14	+ .10	+ .65	— .04
Pb — Cu . . .	....	— .10	0	— .25	+ .04	0	0
Cu_1 — Hg . .	— .19	— .27	+ .01	....	— .03	0	— .25
Co — Hg . . .	....	— .05	+ .01	+ .48	— .01	....	— 1.00
Pt_1 — Cu . . .	....	— .15	+ .03	— .06	+ .17	0	— .31
Pt_2 — Cu . . .	....	— .56	0	— .10	— .16	+ .70	0
Sn_1 — Cu . . .	....	— .04	+ .04	— .29	+ .12	+ .06	0
Mg — Cu . . .	....	+ .18	0	+ .15	— .52	+ .17	0
Al — Cu . . .	....	+ .16	0	+ .12	— .24	+ .18	0
G. s. — Cu . .	....	+ .07	— .01	+ .08	....	....	+ .05
Average . . .	— .16	+ .08	+ .01	+ .03	— .02	+ .14	— .27

LOGARITHMIC EQUATION. DATA — EQUATION IN PER CENT.

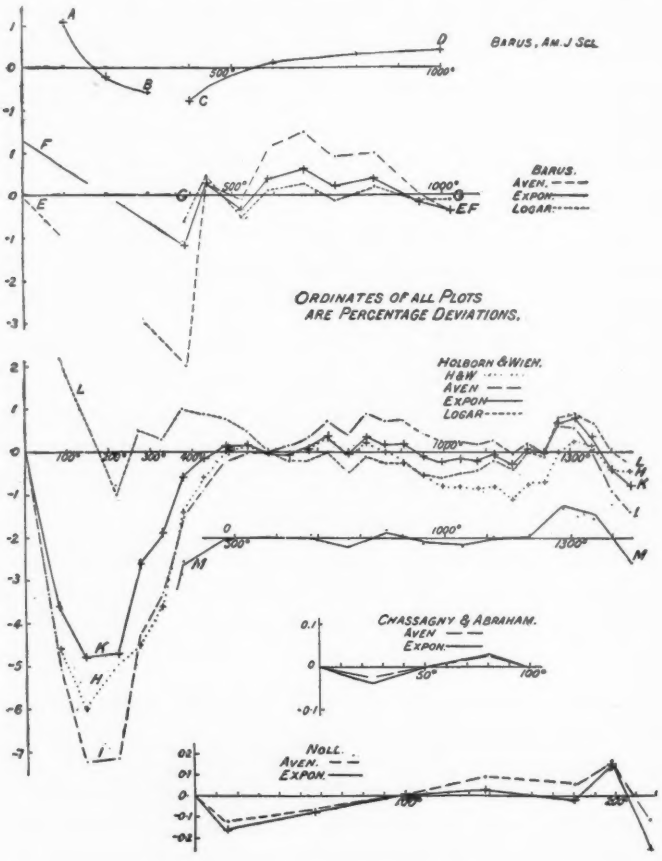
Cu_1 — Hg . . .	+ 2 3	+ 1.5	0.	— 0.4	0.	+ 0.5	+ 0.8

the Barus data), these plots, whether the equation is the ordinary parabolic, the Avenarius, the Barus, the exponential, or the logarithmic, have the same general form, which may be imperfectly described as follows: If the equation be made to conform to the data at 0° C., and at two higher points *a* and *b*, then the deviation will be of the negative sign from 0 to *a*, positive from *a* to *b*, and negative above *b*. The slight departures from this general form are clearly due either to accidental errors or to failure to make the equation conform to the data at all three points, or at suitable ones. The evidence is, therefore, conclusive that *for all of the expressions the deviations are systematic, and not purely accidental in character.*

One of two inferences is, therefore, warranted:

1. *That neither the parabolic, Avenarius, Barus, exponential, nor logarithmic equation is the natural expression of the function.*

2. Or that the scale of temperature to which the values of t are referred in the foregoing investigations departs from the normal scale



by an amount and system roughly indicated by the above residual plots.

The latter inference, suggested by Chassagny and Abraham in the interpretation of their results, does not seem to possess much weight, notwithstanding the urgent need of renewed elaborate experimental

investigation of the relation between the hydrogen, air, and thermodynamic scales of temperature.

As to the relative usefulness of the various expressions for purposes of interpolation and extrapolation some further inspection is necessary. The Barus equation 3, line *C D*, shows slightly smaller deviations on the plot than do the Avenarius and exponential (lines *E E* and *F F*). This, however, is due to the fact that the data against which equation 3 is tested are mean interpolated values, and hence have a sensibly less variable error than those against which the other equations are tested. An approximate exponential equation showed less deviations than equation 3 against the same data. There seems, therefore, to be no advantage in this equation sufficient to offset the difficulty of evaluation of its constants.

Applied to the Barus data from 350° to 1,250°, the exponential equation shows deviations considerably less than one half as great as those of the Avenarius, while those of the logarithmic equation are so small as to lie far within the range of the variable errors, and they, moreover, show no clear evidence of systematic error between these limits of temperature. *For interpolation in the Barus data, therefore, the logarithmic equation is far preferable*, and must be conceded to be representative of the data. For extrapolation it is undoubtedly better than the Avenarius, which (as would the exponential in less degree) would certainly above 1,000° give extrapolated values of Σe too large, or of t too small. The advantage due to its simplicity is also to be noted.

Applied to the Holborn and Wien data from 400° to 1,450°, the exponential equation shows (line *K K*) the same sort of superiority to both logarithmic (line *L L*) and Avenarius (line *I I*) that the logarithmic shows to the others over the Barus data, but in a still more marked degree. Within the limits 450° to 1,450°, in fact, the distribution of the residuals to the exponential is such as not to warrant of itself alone any inference of systematic departure, especially when the mean line *M M* from all the couples. It will be noted as an important confirmation of both the exactness of the electrical measurements in the investigation and the applicability of the exponential formula through a considerable range of alloys (and therefore of values of m and n) that this mean line *M M* is almost identical in form with the line *K K* for alloy A. Relatively to the Holborn and Wien formula (line *H H*), the exponential possesses a similar advantage, with also the merit of greater simplicity of form.

It may, therefore, be affirmed that *for interpolation between 450° and 1,450° in the Holborn and Wien data the exponential equation is abundantly exact. For extrapolation* above 1,450° it would not be entirely safe, although presumably better than the others, since the departure between 0° and 450° and the similarity of the form to others render a systematic departure sufficiently certain.

Applied to the Chassagny and Abraham data (0°–100°), and to the Noll data (0°–218°) (see plots) the Avenarius and exponential formulæ show about equal deviations, but with the advantage slightly on the side of the former. In the case of the Noll data the line indicates that the systematic error is slightly greater for the exponential than for the Avenarius expression. The average deviations in Table IX, on the contrary, show that for each individual equation the concordance is greater for the exponential than the Avenarius. This discrepancy is due to the fact that in order to eliminate local accidental errors the equations (both Avenarius and exponential) are not all made to coincide with the data at the same temperatures, so that the process of averaging by which the data for the Noll plots is obtained is not numerically rigid. This does not, however, sensibly affect the general form of the curve. The greater ease of computation of the numerical constants of the Avenarius expression, and its applicability where both t and t_1 change, ought not to be overlooked. For extrapolation the exponential would be safer, for the reason that it has been above shown that for long ranges its systematic error is less.

The logarithmic equation fits the Noll data very badly, as shown by the deviation in Table IX (not plotted), and also is much less close to the Chassagny and Abraham data than are the others.

The General Conclusion as to applicability, then, seems to be that, while the *Avenarius* expression may be equally good or better than the exponential *for interpolation over short ranges*, yet *for interpolation over long ranges, and for extrapolation above the observation limits, the exponential is decidedly preferable.* The exponential form is also preferable to the remaining expressions, with the exception noted.

The logarithmic form, although closely applicable to the Barus data, is of more doubtful general value, yet on account of its great convenience it may find application in industrial pyrometry as already indicated. Although failing below 300° or 400°, it may probably be applied to the irido- or rhodo-platinum couple between 400° and

TABLE X.

BARUS MELTING AND BOILING POINTS.

	Computed by		Data by Other Observers.	
	Equation 3.	Logarithmic equation.		
Mercury (B. P.) . . .	357°	359°	356°.76	Callendar.
Zinc	420	423	417.57	Callendar and Griffiths.
Sulphur (B. Pt.) . . .	446	449	444.53	Callendar and Griffiths.
Aluminum.	638	641	635	LeChatelier.
Selenium (B. Pt.) . .	694	697	....	
Cadmium (B. Pr.) . .	782	782	....	
Zinc (B. Pt.)	929	926	930	Deville and Troost.
Silver	986	985	968	Holborn and Wien.
	....	....	954	Violle.
Gold	1 091	1 090	1 072	Holborn and Wien.
	....	....	1 035	Violle.
Copper	1 096	1 095	1 082	Holborn and Wien.
	....	....	1 054	Violle.
Bismuth	1 435	1 441	....	
Nickel	1 476	1 485	1 450	Carnelly and Williams.
Palladium	1 585	1 597	1 500	Violle.
Platinum	1 757	1 783	1 775	Violle.

1,200° C., with a maximum error not exceeding about 5°. If extended to cover 400° to 2,000°, the error might rise to 15° or 20°.

More in detail, it may be briefly noted by way of summary:

That the logarithmic equation fits the Barus data between 400° and 1,250° with scarcely sensible systematic error and within the limits of variable errors of the data;

That the exponential equation similarly fits the Holborn and Wien data within the limits 400° to 1,445°;

That when made to coincide with the data at about 450° and 1,200°, the systematic deviations of the exponential equation from the Barus data, and of the logarithmic equation from the Holborn and Wien data, are in general of opposite sign and of roughly equal magnitude.

Barus Melting and Boiling Point Data.

From the foregoing demonstration of its applicability, it seems proper to apply the logarithmic formula to the Barus thermo-electric data on melting points.[1]

Whether the extrapolation above 1,000° by the logarithmic formula is entitled to any great weight may be questioned, but there is no obvious reason why it is not more reliable than by any of the others. I have employed the equation given on a preceding page, which represents very closely Barus' high temperature air thermometer comparisons, calculating thence the temperatures t corresponding to the values of $\Sigma_{20}^{t}e$ given by Barus for the various points, assuming Barus' value $\Sigma_{o}^{20}e = 150$ mv. The results are given in Column 3 of Table X. Column 4 quotes the most reliable previous determinations of the same points by other observers. As to which of the two columns of results best represents Barus' work, there can be little doubt from the above evidence that below 1,000° it is the second, that is, the one computed from the logarithmic equation. These combine both his own air thermometer and melting point work. Above 1,000° the logarithmic values are probably slightly too high.

Remarks.

Review of the laborious researches which have been devoted to the direct comparison of thermo-electric elements with the air thermometer, mainly for the purpose of advancing the art of pyrometry, has enforced the conviction that, at least for the immediate future, this end would be better served by accurate gas thermometer measurements of melting points of metals. Each such determination made upon a reproducible metal of known high purity under proper reproducible conditions fixes an enduring and reproducible reference point, a pyrometric "bench mark." And there are enough inexpensive metals, together with a possible system of simple alloys, to give points of sufficient frequency. These would then afford a convenient means of obtaining accurately known high temperatures for purposes of study of all high temperature phenomena, and particularly for calibrating thermoelectric, electrical resistance, optical, or other secondary pyrometric interpolation apparatus, for it must be remembered that all

[1] Barus, American Journal of Science. *Vide ante.*

such apparatus is necessarily secondary, the gas thermometer being inevitably the primary.

On the other hand, comparison with the air thermometer, of a thermo-couple or of a resistance pyrometer, or the study of any progressive thermal phenomenon, while it possibly may result in the eduction of a natural law, is very unlikely to lead to anything more than the establishment of an approximate equation, with constants characteristic only of the individual materials actually employed, and not transferable to other, although similar, materials. Such results are obviously of a much more ephemeral character than the melting point measurements. Even when any pyrometric apparatus thus tested is applied to the establishment of melting points, it must at best yield results inferior to the direct application of the gas thermometer, except in cases where the latter is hampered by want of sufficient quantity of the metal to be experimented upon, a condition which need only affect such costly substances as gold and platinum.

Stated broadly, the great need of the art of pyrometry is convenient methods of producing, or of recognizing when produced, a series of accurately known high temperatures. The analogous problem has been partially solved for thermometry at temperatures up to 300° C. by the investigation of boiling points of certain chemically pure substances under controlled pressure.

TREATMENT OF ROASTED GOLD ORES BY MEANS OF BROMINE.[1]

By RICHARD W. LODGE.

Received September 25, 1895.

Mr. H. R. Batcheller, of the class of 1894, Massachusetts Institute of Technology, while experimenting with chlorine gas on a certain lot of roasted concentrates, met with the following difficulties: 1. A poor extraction of the gold. 2. A very large consumption of chlorine gas. 3. Inability to precipitate all of the gold from the solution containing the $AuCl_3$. 4. The bullion obtained was very base.

These difficulties were the same whether the chlorine was generated from H_2SO_4, MnO_2, and salt, or whether H_2SO_4 and bleaching powder were used. They may be accounted for partly by the presence of some arsenic left in the roasted ore, and partly by the presence of copper in the solution containing the $AuCl_3$.

It was therefore suggested to try the effect of bromine on a similar lot of ore. The use of this element is, of course, nothing new, but in the following experiments it seemed to present many advantages over chlorine.

The material worked upon consisted of some concentrates containing 2.31 ounces of gold per ton and 34.26 per cent. of arsenic, which would correspond to about 74.4 per cent. of arsenopyrite. Considerable pyrite and a small amount of galena and chalcopyrite were also present.

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[1] Reprinted from Transactions of the American Institute of Mining Engineers. Florida Meeting, March, 1895.

The material when sized and assayed showed:

	Per cent.	Ounces gold per ton.
On 24-mesh sieve	.7	Assaying 1.4
On 30-mesh sieve	1.9	
On 40-mesh sieve	3.5	Asssaying 1.2
On 50-mesh sieve	6.0	
On 60-mesh sieve	4.5	Assaying 1.12
On 80-mesh sieve	11.0	Assaying 1.19
On 100-mesh sieve	26.0	Assaying 1.4
Through 100-mesh sieve	45.0	
Loss	1.4	
	100.0	

The line of treatment was as follows:

1. Roasting the concentrates in a reverberatory furnace.

2. Submitting the roasted ore to bromination in strong preserve jars, "lightning brand," with double gaskets, the jars and their contents being revolved during the experiment.

3. Precipitation of the gold by means of H_2S:

ROAST I. — Time, five hours.

	Kilos.	Assay. Ounces gold.
Raw ore	10	2.31
Roasted ore	6	3.36
	Per cent.	Per cent.
Loss	40	12.7

BROMINATION.

Roasted ore	500 grammes.
Bromine	14.5 cc.
Water	500 cc.
Time	5½ hours.

Assay of tailings from two tests gave 0.30 and 0.32 ounces of gold. Based on the roasted ore, this would be an extraction of 90.7 per cent.

ROAST II. — Time, eight hours.

	Kilos.	Assay. Ounces gold.
Raw ore	15	2.31
Roasted ore	8	4.29
	Per cent.	Per cent.
Loss	46.67	1

The following experiments were made to determine the proper amount of bromine for 500 grammes of ore:

Roasted ore. (Grammes)	Bromine. (CC.)	Time. (Hours.)	(Water. (CC.)	Extraction, based on assay of tailings. (Per cent.)
500	3 0	5½	500	90.67
500	3.0	5½	500	89.27
500	1 5	5½	500	92.54
500	1.0	5½	500	81.35
500	0.5	5½	500	62.23
500	0 3	5½	500	60.00

The following were made to determine the shortest period of contact of ore and bromine giving a good extraction:

Roasted ore. (Grammes.)	Bromine. (CC.)	Time. (Hours.)	Water. (CC.)	Extraction, based on tailings. (Per cent.)
500	1.5	5½	500	92.54
500	1.5	4½	500	88.00
500	1.5	3½	500	86.00
500	1.5	2	500	81 35
500	1.5	1	500	72.02

These tests seem to indicate that 1.5 cc. of bromine, added to 500 grammes of ore in 500 cc. of water, would effect in five and one half hours an extraction of over 90 per cent. of the gold in the ore.

To test these conclusions, a third roast was made:

ROAST III. — Time, eight hours. (Ore cooled in furnace.)

	Kilos.	Assay. (Ounces.)	Arsenic. (Per cent.)	Sulphur. (Per cent)
Raw ore	70	2.31	34.26	....
Roasted ore . . .	43.7	3.58	0.11	0.34
	Per cent.	Per cent.		
Loss	37.6	$3\frac{3}{10}$	99.67	....

Of this roasted ore, 15 kilos were treated with 45 cc. of bromine in 15 kilos of water for four and one half hours in a revolving keg. The tailings showed an extraction of 85.5 per cent.

As an excess of bromine was present when the keg was opened, at the end of four and one half hours, a second experiment was tried with ore, 15 kilos; bromine, 35 cc.; time, five and one half hours; water, 15 kilos.

This showed an extraction of 92.18 per cent., based on the assay of the tailings. The actual gold recovered from the solution was only about 80 per cent., which may be accounted for by the presence of considerable copper in the solution.

The expulsion of the bromine from the solution seemed to be best brought about by means of SO_2. Air and steam were both tried, but with poor success. After the passage of SO_2 the solution was quite clear, although some gold would be precipitated on standing.

When the ore was chlorinated the solution at this point, containing the $AuCl_3$, would be quite turbid, and evidently contained a large amount of base metals as chlorides. These would necessarily interfere with the complete precipitation of the gold, besides making the bullion base. Some base metals, such as copper, were also present in the bromine solution, but apparently not to such an extent, for the solution was clear.

The gold was finally precipitated by means of H_2S.

In the experiments on this particular ore bromine seemed to have the following advantages over chlorine:

1. It extracted a much higher percentage than chlorine, the results being estimated not only on the assay of the tailings, but also on the actual gold recovered.

2. It gave solutions much more free from base metals. This would be expected, especially where chlorine is generated by means of H_2SO_4 and bleaching powder, and the acid has a chance to act directly on the ore.

3. Less time is required to extract the gold.

4. The ease in using and comfort in handling is much greater.

As regards the comparative cost, the least amount of bromine which could be used on this ore with a successful extraction appeared to be 0.3 per cent., or 6 pounds per ton. With bromine at 25 to 40 cents per pound, this would make the cost very high; but the cost of chlorination would certainly be still higher, as it was found necessary to use as high as 10 per cent. of lime and 6 per cent. of H_2SO_4 to obtain even a fair extraction.

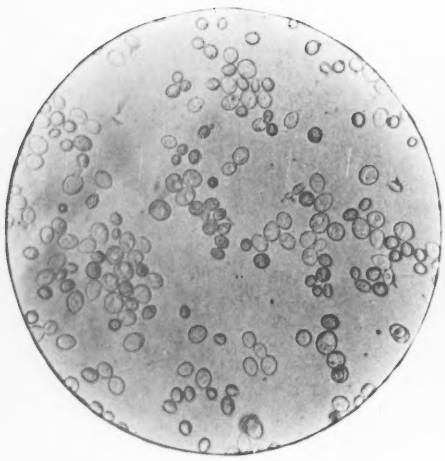


Fig. 2.
SACCHAROMYCES CEREVISIÆ.
(Beer yeast.)
× 300.

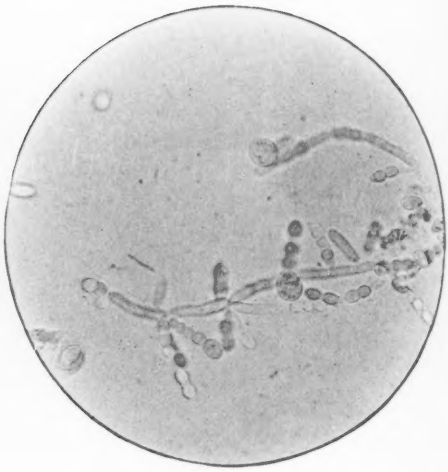


Fig. 3.
SACCHAROMYCES PASTORIANUS SHOWING SPORES.
(Wild yeast.)
× 600.

Fig. 4.
SACCHAROMYCES CEREVISIÆ SHOWING SPORES.
× 600.

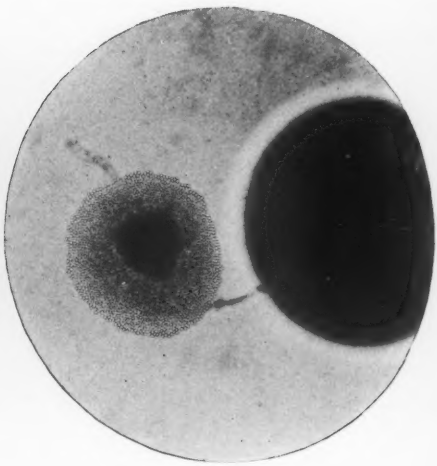


Fig. 5.
COLONY OF YEAST ON WORT GELATIN.
× 40.

ON PURE YEAST AND HANSEN'S METHOD FOR ITS CULTIVATION.

By SIMEON C. KEITH, Jr., S.B.

Read April 25, 1895.

Since the time of Pasteur's famous researches on fermentation there has been a more or less general adoption of the microscope and of scientific methods in brewing and other fermentation industries.

About 1880 Jacob C. Jacobsen, a wealthy and intelligent Danish brewer, realizing the importance of investigations upon yeast and the brewing process, established a special research laboratory in connection with his Carlsberg Brewery at Copenhagen, with Dr. Kjeldahl as chemist and Dr. Emil Christian Hansen as biologist.

Early in his scientific investigation Hansen found that many of the beers which had contracted "disease" were not, as Pasteur had supposed, suffering from invasions of bacteria, but, on the contrary, from yeast cells of another sort than those characteristic of sound fermentations. These foreign yeast cells (wild yeast) were of a somewhat different shape, and different in other respects, also, from those found in normal fermentations. (See Figures 2, 3 and 4.) At the same time he became interested in observing the sporulation of yeast cells, and found that the time of spore formation varied greatly with different yeasts. This was especially true when they developed at either a high or a low temperature.[1] He found, furthermore, that spore formation was favored if the cells were young and vigorous, and also if there was a plentiful supply of atmospheric oxygen. Following out this idea he devised a method of yeast analysis by which he showed that his "disease producing" yeasts consisted of more than one spe-

[1] For Saccharomyces Pastorianus I. (a species of wild yeast) the maximum and minimum temperatures at which spores develop are, respectively, 30°.5 C. and 4° C. The time required for the production of spores at the former temperature is 30 hours, and at the latter temperature 14 days. With an ale yeast the maximum and minimum temperatures of spore formation are 36° C. and 12° C., and the respective times required are 29 hours and 10 days. (Figures 2 and 3.)

cies, although microscopically they might have appeared to be the same. Sometime afterward the same was found to be true with brewers' yeast, and here the species also manifest themselves in the quality of the beer produced. Some yeasts produce beers of good flavor, while others give undesirable flavors; some give a high percentage of alcohol and some a low percentage, and so on. The conclusion was obvious, namely, that in order to get the best product not only a yeast free from disease yeasts and bacteria, but a carefully selected species of yeast must be employed.

In order to secure such a pure culture of yeast, Hansen in his first investigations (1880) used the dilution method of Lister, which is briefly as follows: The yeast from which the culture is to be made is carefully diluted in a flask of sterilized water, so that there shall be about one yeast cell to each two drops of water. To do this the number of cells in a drop of rather highly diluted yeast is counted under the microscope, a drop of this mixture then placed in twice as many drops of sterilized water as there are yeast cells, and after shaking violently, so as to separate the cells, one drop is placed in each of twenty-five Freudenreich flasks of sterilized wort. The flasks are next allowed to remain three or four days undisturbed, and if they are then examined small white specks will be seen on the bottom of some of them; these are colonies of yeast, and have grown from the cells introduced with the single drop. The flasks containing one speck are presumably pure cultures; but since in some instances two cells of different varieties might stick together and form an apparently homogeneous colony, one could never be absolutely sure of the purity of the culture.

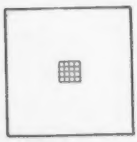


FIG. 6. ETCHED COVER SLIP USED IN COUNTING YEAST CELLS.

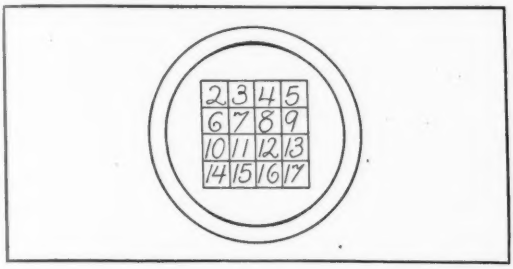
In 1881 Koch introduced the use of solid culture media into bacteriology, and Hansen soon after employed it in a unique modification of the plate method for making pure cultures of yeast in such a way as to avoid all possibilities of error. Absolutely pure cultures are secured without difficulty by making use of a modification of the Böttcher moist chamber in which the thin cover has sixteen small numbered squares etched upon it. (Figure 7.)

The yeast from which the pure culture is to be made is largely diluted in sterilized wort gelatine,[1] and a thin layer is spread on the

[1] Beer wort containing from 5 per cent. to 10 per cent. of gelatine.

Fig. 1. Pure Culture Apparatus.

inner side of the cover of the Böttcher chamber. When the gelatine solidifies, the yeast cells become fixed in position, and the location of the well-isolated single cells is noted on a corresponding diagram, so



a — Cover slip.
b — Layer of wort gelatine containing yeast cells.
c — Drop of water.

FIG. 7.
HANSEN CULTURE CELL.

that the yeast colonies growing from them may be identified. (Figure 8).

In the course of a week the colonies growing from the single cells will have reached the size of a small pin's head (Figure 5), and now some of the colony which has grown from a single cell is transferred by means of a sterilized wire to a Freudenreich or small Pasteur flask.

After the fermentation is complete in this first flask, the character of the yeast is studied and the quality of the beer which it will produce is determined. That yeast which is best suited to meet the conditions required is allowed to multiply in large Pasteur flasks until by successive cultivations enough pure yeast is finally produced in the copper Carlsberg flask to charge the culture apparatus (Figure 1.) This apparatus was invented by Hansen and Kühle, and is in effect a giant Pasteur flask. It is so arranged that quantities of yeast sufficient to "pitch" eight hectoliters of wort can be generated every ten days. Since a great source of invasion or infection in beers is undoubtedly the use of worts infected by germs from the air, great care is taken that wort free from germs shall be supplied for the development of the pure yeast. This is done in the apparatus by cooling the boiling hot wort in the wort tank (see left-hand tank in Figure 1),

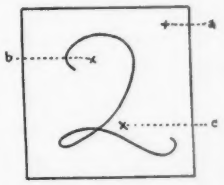


FIG. 8.
Diagram of one etched square, showing how the positions of yeast cells and resulting colonies are located.
a, b, c — Location of single cells.

and at the same time aërating it with air that is freed from germs by being filtered through cotton.

In the Carlsberg Brewery the same principle is applied to cooling the whole of a brewing, so that with proper care the yeast remains in a state of purity for some time after being introduced from the culture apparatus to the brewery. The purity of the yeast is easily tested from time to time by sowing on blocks of plaster of Paris. The wild yeast spores are formed at a temperature of 15° C. in a much shorter time than the spores of culture yeast, so in this way we have a method by which an exceedingly small infec-

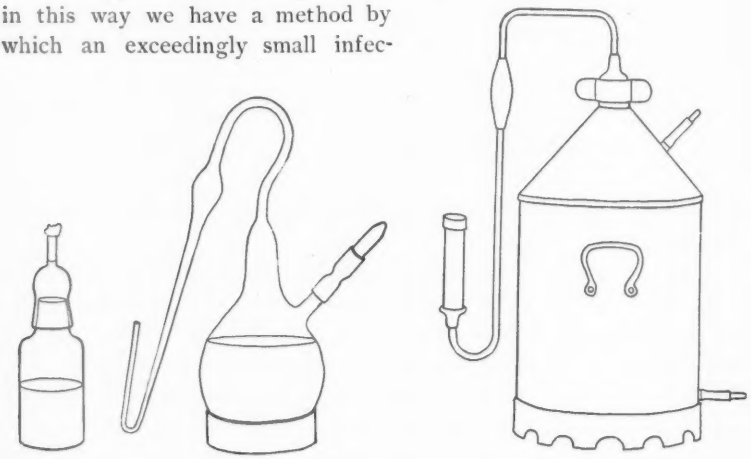


FIG. 9. FREUDENREICH FLASK (× ½).

FIG. 10. PASTEUR FLASK (× ½).

FIG. 11. CARLSBERG FLASK (× ⅛).

tion may be detected. The fermentation room in this brewery is also unique and deserves special notice. The fermenting tubs are made entirely of slabs of slate, and are placed in long, narrow, arched cellars, in single rows on each side, leaving an aisle in the center. Running lengthwise at the top of the arch is a long air conduit with dampers opening in such a way that a jet of cold sterilized air can be blown over the surface of the beer, and thus its temperature kept absolutely under control.

On the death of Jacobsen, in 1887, the control of the Carlsberg Brewery passed by his will to a board appointed by the Royal Danish Scientific Society, and the profits of the brewery are used mainly in aiding scientific research, especially in the line of fermentation.

Within the past two years Hansen has investigated the organisms of acetic acid fermentations, and has added greatly to our knowledge on this subject. Contrary to Pasteur, Hansen finds that there are several closely allied but distinct species of the acetic bacteria, and that the two principal ones can be distinguished by the action of iodine. Iodine gives a blue coloration to *Bacterium Pastorianum*, while *Bacterium aceti* is colored yellowish brown. He has also studied their polymorphism under varying conditions, and finds that the rod or chaplet shape occurs when the bacteria are grown at low temperatures. At 40° C., however, very long swollen cells make their appearance; but this character is not permanent, for if cultures be again made of them at the ordinary temperatures only the former shape is found.

Since the recent studies on the lactic fermentation concerned in butter-making, by Storch, of Denmark, and Conn, of Wesleyan University in Connecticut, use has been made of the Hansen apparatus in the preparation of pure cultures of bacteria particularly adapted to the production of a butter of superior quality, and in Denmark, at least, the bottled cultures of such bacteria are an article of commerce.

From time to time the question has arisen whether yeasts are a distinct class of organisms or only forms of some of the higher fungi. Quite recently an American, John J. Juhler, working under Jörgensen, claims to have found a genetic connection between certain molds and yeast. Under certain conditions he finds that the conidia of a Japanese mold (*Aspergillus oryzæ*) when grown on the surface of sterilized grapes can develop budding cells which have all the characters of true yeast. Jörgensen has confirmed Juhler's experiments, so that there is little reason to doubt that some yeasts, at least, may be derived in this way.

Among the possible uses of pure yeast is its introduction into the baking industry. About a year ago it occurred to me that if a particular variety of pure yeasts is adapted to brewing, we should expect the same to be true in the case of the fermentation of dough in bread-making. Naturally, pure yeast would also have the advantage over the present commercial yeast in that it would be free from lactic-acid bacteria and molds, which, in the summer time, cause great trouble in the production of good bread. With this in view I carried out several experiments in which pure cultures of yeast were used. The material and utensils used in making the experiments were carefully sterilized

in order that the purity of the culture might be maintained during the fermentation of the dough. The results were highly satisfactory, and show that the idea is undoubtedly a correct one; the bread was of superior grade, and its keeping qualities and absence of any acid flavor were especially noticeable. Some experiments were also conducted in order to ascertain whether or not bread was sterilized sufficiently in baking to kill the yeast cells. Several of the breads sold in Boston failed to show any living yeast cells in the interior of even the most slack-baked loaves examined, which shows that in most, if not in all, cases the cells must be killed in the process of baking. This has been denied by some observers.

In the summer of 1894 I had the opportunity of spending a few months at the Zymotechnical Institute at Copenhagen, under its well-known director, Mr. Alfred Jörgensen, and I wish here to express my appreciation of the many favors then shown to me by him.

THE CYANIDE PROCESS AS APPLIED TO THE CONCENTRATES FROM A NOVA SCOTIA GOLD ORE.[1]

By RICHARD W. LODGE.

Received September 25, 1895.

The following work, performed by Mr. W. A. Tucker, of the class of 1893, in the Mining Department of the Massachusetts Institute of Technology, seems to me to be worthy of publication. I believe it has always been considered that the presence of arsenic especially interferes with the extraction of gold by the cyanide method. Mr. Tucker's work, although made on a laboratory scale, certainly seems to disprove this view, and to show that, even with a very large percentage of arsenic present in the ore, a high extraction may be obtained without an excessive consumption of KCy.

The ore from which the concentrates were obtained was a gray argillaceous schist and slate, with stringers and veins of quartz running through it. It carried free gold and about 12 per cent. of sulphides. The ore was crushed with stamps; the free gold was collected in the ordinary way on silver-amalgamated copper plates; and the sulphides, which consisted chiefly of arsenopyrite and pyrite, with very small amounts of galena and chalcopyrite, were concentrated and collected by means of a Frue vanner.

A carefully taken sample gave:

Gold	6.17 ounces per ton.
Arsenic	30.6 per cent.

The latter figure would correspond to about 66.5 per cent. of arsenopyrite in the concentrates.

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[1] Reprinted from Transactions of the American Institute of Mining Engineers. Florida Meeting, March, 1895.

The work to be done was outlined as follows:

1. Sizing the concentrates;

2. Assaying the different sizings;

3. Treating these different sizings with KCy of different degrees of strength for different periods of time.

Owing partly to the small amount of concentrates found on the 40- and 60-mesh sieves, and partly to the lack of time, the following four series were substituted in place of carrying out No. 3.

Series I. — Treating concentrates with a given amount of a 1 per cent. KCy solution for different periods of time. The solution, instead of being all added at once, was added in three portions.

Series II. — Treating a given amount of concentrates with an equal quantity of a 1 per cent. solution of KCy for different periods of time, the KCy not being renewed as in Series I.

Series III. — The same as Series II, except that the concentrates were revolved with the KCy solution in bottles, and did not simply stand in contact with it, as in the previous series.

Series IV. — Concentrates and solution in motion; strength of KCy solution, time of contact and amount of solution varying.

Sizing and Assaying Concentrates.

A sample of the concentrates sized and assayed resulted as follows:

Sieve Mesh.		Proportion of sample. (Per cent.)	Assay. (Ounces per ton.)	Gold.	Proportion of total gold. (Per cent.)
Through.	On.				
	40. . . .	0.412	25.70	0.000363	1.71
40	60. . . .	0.449	27.10	0.000417	1.96
60	80. . . .	4.010	10.69	0.001468	6.90
80	.....	92.710	6.00	0.019005	89.43
Lost		2.419	.....	.....	.....
Total		100.000	.....	0.021253	100.00

The above assays include, of course, the free gold (pellets) which may have been found on the 40-, 60-, and 80-mesh sieves.

Treatment with Cyanide.

Series I. — One A. T., or 29.166 grammes, of concentrates passed through a 30-mesh sieve, and assaying 6.17 ounces per ton, was treated with 100 cc. of KCy (1 per cent.) solution. This solution was added at three different times in equal portions, the first portion being drawn off before the second was added, and so on.

The apparatus employed was an inverted glass bottle, with the bottom cut off, and a perforated porcelain plate laid across at the point of contraction to the neck, so as to form (in the inverted position) a false bottom. Below this, the neck was closed with a rubber stopper, through which passed a glass tube, fitting outside to a rubber tube, closed with a pinch-cock.

The result of these tests was as follows:

Time of adding KCy, calculated from first addition.		Time of withdrawing the third addition of KCy. (Hours.)	Assay of tailings in ounces per ton.	Percentage of gold extracted.	Grammes of KCy consumed.	Grammes of KCy used per gramme of gold extracted.
Second. (Hours.)	Third. (Hours.)					
16¼	20½	23	1.92	68.88	0.112	26.4
16¼	20½	23	2.39	61.26	0.124	32.8
23½	30	51	1.43	76.82	0.168	35.4
22½	29½	51	2.82	54.29	0.146	43.6
23	65	70	1.44	76.66	0.155	32.8
23	65	70	2.78	54.94	0.156	46.0
24	44	94	1.51	75.52	0.169	36.3
24	44	94	2.67	56.72	0.206	58 9
24	44	94	1.51	75.52	0.165	35.4
20½	94½	118	1.62	73.74	0.164	36.0
20½	94½	118	1.56	74.72	0.202	43.8
20½	94½	118	1.23	80.06	0.202	40.9

These results were not at all satisfactory, for they neither indicated that the extraction increased with the time of contact, nor did they show in what period of the contact the solution of the gold took place.

Series II. — The apparatus used was the same as in Series I. Quantity of concentrates (through 30-mesh), 25 grammes; assay, 6.17 ounces per ton; quantity of KCy (1 per cent.) solution, 25 cc. The solution was not changed.

These experiments seem to show that the extraction of gold increases with the time of contact of the KCy. Apparently, the consumption of KCy increases with the time. This large consumption in both Series I and II is no doubt due to the free access of air to the apparatus in which the tests were made.

Duration of treatment. (Hours.)	Assay of tailings. (Ounces per ton.)	Per cent. of gold extracted.	Grammes of KCy consumed.	Grammes KCy used per gramme of gold extracted.
16	2.97	51.84	.064	23.4
16	2.75	55.43	.065	22 2
22	2 30	62.72	.058	17.5
22	2.17	64.83	.058	16.9
25½	2.12	65.64	.065	19.6
71	2.51	59.32	.124	39.5
71	2.24	63.69	.118	35.0
71	2.57	58.35	.127	41.1
118	1.61	73.91	.091	23.3
118	1.40	77.31	.131	32.5
118	1.26	79.58	.134	31.1

While working on these experiments, 25 grammes of concentrates and 25 cc. of KCy solution were put in a bottle, tightly stoppered, which was caused to revolve. The extraction was such an improvement on all the previous work that all other experiments were conducted in this way.

Series III. — Quantity of concentrates (through 30-mesh), 25 grammes; assay, 6.17 ounces per ton; quantity of KCy (1 per cent.) solution, 25 cc. Bottles and contents revolved.

Duration of revolution. (Hours.)	Assay of tailings. (Ounces per ton.)	Per cent. extracted, calculated from No. 2.	Grammes of KCy consumed.	Grammes of KCy used per gramme of gold extracted.
2	0.39	93.68	0.022	4.44
2	1.11	82.01	0.033	7.60
2	0.82	86.71	0.035	7.63
2	0.82	86.71	0.032	6.97
4	0.66	89.30	0.072	15.25
4	0.62	89.95	0.042	8.82
5¼	0.58	90.60	0.053	11.06
5¼	0.47	92.38	0.063	13.07
23	0.42	93.19	0.031	6.42
23	0.58	90.60	0.043	8.98

These experiments seem to indicate that to revolve the bottles about six hours was sufficient, and that the extra amount of gold extracted would hardly compensate for a longer revolution.

Series IV. — Bottles and contents revolved.

CONCENTRATES THROUGH 30-MESH; ASSAY, 6.17 OUNCES PER TON.

Duration of revolution. (Hours.)	Weight of ore. (Grammes)	Strength of KCy. (Per cent.)	Quantity of KCy Solution. (cc.)	Assay of tailings. (Oz. per ton.)	Per cent. of gold extracted.	Grammes of KCy consumed.	Grammes of KCy per gramme of gold extracted.
4	50	1.0	25	0.87	85.90	.026	2.84
4	50	1.0	25	0.71	88.49	.094	10.03
4	25	0.5	25	0.47	92.38	.014	2.86
4	25	0.5	25	0.66	89.30	.009	1.91
4	25	0.5	25	0.89	85.57	.014	3.09
16½	25	0.5	25	0.97	84.28	.055	12.33
16½	25	0.5	25	0.57	90.76	.050	10.42
23	25	0.5	25	0.51	91.73	.045	9.28

CONCENTRATES THROUGH 80-MESH; ASSAY, 6 OUNCES PER TON.

Duration of revolution. (Hours.)	Weight of ore. (Grammes)	Strength of KCy. (Per cent.)	Quantity of KCy solution. (cc.)	Assay of tailings. (Oz. per ton.)	Per cent. of gold extracted.	Grammes of KCy consumed.	Grammes of KCy per gramme of gold extracted.
6¼	1,000	1.0	1,000	0.70	88.30	7.033	77.06
6½	1,000	0.5	1,000	1.00	83.33	3.617	40.22

The large consumption of KCy in these last two tests was due to insufficient washing.

In none of the tests were the concentrates washed with water previous to their treatment with cyanide. Owing to lack of time, Mr. Tucker was unable to test the solutions for arsenic, or to see whether all the gold could be recovered from them; so we are unable to give any data on these points. While we realize that these are simply laboratory experiments, that the tailings are in all cases too rich to be thrown away, still we consider the extraction remarkably high on material carrying the percentage of arsenic that this does. Making the tests in a closed vessel lessens the consumption of KCy, as one would expect. As the extraction also increases, this would seem to be contrary to Elsner's equation, to which oxygen is necessary; and certainly there could hardly be enough in a small bottle to influence the extraction. Keeping the ore and solution in agitation certainly seems to have helped the extraction, although this method of working has met with very little success in actual practice.

REVIEW OF AMERICAN CHEMICAL RESEARCH.

General and Physical Chemistry.

A. A. Noyes, Abstracter.

The Chemical Kinetics of Oxydation. By Herman Schlundt and Robert B. Warder. **I. On the Speed of the Liberation of Iodine in Mixed Solutions of Potassium Chlorate, Potassium Iodide, and Hydrochloric Acid.** By Herman Schlundt. *Am. Chem. J.*, 17, 754–770. — The title sufficiently indicates the character of the investigation. The results are expressed both numerically and graphically. The authors' conclusions are, first, that the velocity increases greatly with increase of temperature and of concentration; second, that the effect of an excess of potassium iodide is about the same as that of an equivalent excess of potassium chlorate; third, that an equivalent excess of acid causes a much greater increase of speed; fourth, that hydrobromic, hydrochloric, nitric, and sulphuric acids accelerate the reaction in a greater degree in the order named. The difference in effect of the first three was quite small, however. The abstracter considers the second conclusion of importance; for it shows that the reaction, aside from the accelerating effect of acid, is one of the second order, like the analogous reactions with potassium iodide and hydrogen peroxide or bromic acid recently investigated (*Ztschr. physik. Chem.*, 18, 122).

An Early American Arrangement of the Elements. By F. P. Venable. *J. Am. Chem. Soc.*, 17, 947–949. — The author calls attention to the fact that L. R. Gibbes, of Charleston, South Carolina, published in 1875, evidently in ignorance of the tables of Mendelejeff and Meyer, an arrangement of the elements presenting many of the essential features of the periodic law.

Some Additional Notes on Argon and Helium. By Edwin A. Hill. *Am. J. Sci.*, 50, 359–376. — The author supports his previously expressed opinion (*Tech. Quart.*, 8, 307), that the molecule of argon is diatomic, by a lengthy discussion of the significance of its inertness, in which he attempts to disprove the hypothesis that argon, like mercury, at 800° is above the temperature at which chemical combination is possible, by showing that the elements with which it possesses the closest (physical) analogies — the gaseous elements — are below the temperature of greatest chemical activity, and by pointing out that the few cases in which it has been made to combine are all attended with a great expenditure of external energy. Its inertness has, in the abstracter's opinion, little or no bearing on the question, inasmuch as this property seems most probably to be one inherent in the argon *atom*; for it is to be remembered that by far the most conclusive evidence of its inertness is the fact that no compounds of it have been found to exist in nature, showing that neither the varied conditions that now exist nor the high temperature

conditions of the past have given rise to the formation of compounds. — The latter portion of the article is devoted to a summary of the recent publications concerning argon and helium.

The Rate of Hydrolysis of Salicine with Acids. By Arthur A. Noyes and William T. Hall. *Tech. Quart.*, **8**, 288–293. — The authors show by polariscopic measurements that the rate of hydrolysis of salicine into dextrose and saliretine at 95° is expressed by the equation of the first order: $dx : dt = c(A - x)$ and that the relative catalytic effects of hydrochloric, sulphuric, oxalic, and malonic acids on this reaction are approximately the same as those on the sugar inversion.

H. M. Goodwin, Abstracter.

The Chemical Potential of the Metals. By Wilder D. Bancroft. *Proc. Am. Acad.*, **31**, 96–122; *Phys. Review*, **3**, 250–269. — This paper contains the results of some original experiments on the electromotive force of non-reversible elements and a discussion of the results of others on similar cells. A new theory of the factors determining the potential difference between metals and electrolytes is expounded, which is essentially stated in the following quotation of the first two conclusions of the paper: "1st. The potential difference between a metal and an electrolyte is not a function of the concentration of the salt solution, nor of the nature of the positive ion, except in certain special cases. 2d. It is a function of the electrode, of the negative ion, and of the solvent." These conclusions and those following, deduced, as they are, from experiments on polarizable cells, would, were they confined to such cells alone, merit at least serious consideration and criticism, but when extended to include *reversible* electrodes, the theory of which has been so fully developed and completely verified by experiment in the last few years, the disagreement between the author's theory and the facts is so obvious as to make a detailed criticism seem superfluous. One case may be mentioned which will serve to show the fallacy of the author's views. According to his theory, the electromotive force of the reversible elements, Zn | $ZnCl_2$ | $ZnBr_2$ | Zn and Zn | $ZnCl_2$ | ZnI_2 | Zn, the solutions being of equal concentration, say 0.1 normal, and the salts assumed equally dissociated, should be 0.080 and 0.152 volt, respectively. As a matter of fact the electromotive force of both these elements is practically zero (actual measurement by the abstracter gave 0.002 and 0.003 volt), a result inexplicable if the potential difference depends on the nature of the halogen ions, but in complete agreement with and a necessary consequence of Nernst's theory of the voltaic cell, according to which it is primarily a function of the kation concentration, which in all of the above solutions is practically the same. Had the author but taken the trouble to make one or two experiments to test the above conclusions, which he himself draws, he would have convinced himself of the fallacy of his views, and thus saved himself the trouble of much of the criticism of the work of others contained in his paper.

On the Formation of Layers in Mixtures of Acetic Acid and Benzene. By C. E. Linebarger. *J. Am. Chem. Soc.*, **17**, 932–933. — The author finds that when care is taken to obtain absolutely pure products a mixture of benzene and acetic acid when cooled to —20° C. shows no indication of layer formation as described by Duclaux. This is in complete agreement with the author's previous experiments, and the results of Duclaux are undoubtedly to

be explained by the fact that he used incompletely dehydrated acetic acid, and thus experimented with a ternary mixture of water, acetic acid, and benzene, instead of a binary mixture of the last two. The author finds that it requires only a slight addition of water to affect the separation usually observed.

A Remarkable Electrolytic Phenomenon. By C. J. Reed. *J. Franklin Inst.*, **139**, 283–286. — When a solution of disodium hydrogen phosphate is electrolyzed between lead electrodes, and the negative electrode taken so small as to insure a very great current density, a voluminous cloud of dark blue heavy precipitate is formed at this electrode. The precipitate when washed and dried was found to be a permanent impalpable powder resembling lead, but showed no luster on grinding in a mortar. Heated in air to the melting point of lead, it combined with oxygen with incandescence, forming yellow lead oxide. Heated out of contact of air, it melted to metallic lead. The precipitate was found to be formed when a number of other solutions were electrolyzed under the same conditions: solutions of salts of metals which can be deposited electrolytically and of strong acids formed exceptions. Of the metals, arsenic alone showed the same behavior as lead. No figures are given in regard to the voltage, current, or current density used.

The Relationship of the Heat of Vaporization of Gases to Their Density and also to Their Boiling Point. By William L. Dudley. *J. Am. Chem. Soc.*, **17**, 969–986. — The article consists mainly of a number of plots in which the values of the "latent heat of one cubic centimeter of vapor (reduced to 0° and 760 mm.)" for different liquids are plotted as ordinates against their densities referred to hydrogen and absolute boiling points as abscissæ. From the general linear form of the resulting curves the author enunciates the "law" that in any homologous series the heat of vaporization in a unit of volume of the vapor, under the same conditions as to temperature and pressure, is proportional to the density, and also to the absolute boiling point. The author's computation of latent heat of 1 cc. of vapor seems to the abstracter erroneous, since the specific gravity of the *liquid* should be entirely omitted from his formula. The proportionality between molecular heats of vaporization and absolute boiling point, which, if Avogadro's law is admitted, is but another expression of the above enunciated law, has long been known as Prouton's Law.

Preliminary Table of Solar Spectrum Wave Lengths. By Henry A. Rowland. *Astro phys. J.*, **2.**, 306–315, 360–369. (*See Tech. Quart*, **8**, 94, 312.) — The above references contain measurements of wave lengths from 5429.349 to 5913.930.

On the Wave Length of the D_3 Helium Line. By A. DeForest Palmer, Jr. *Am. J. Sci.*, **50**, 357–358.

On Some Devices for the Separation of Minerals of High Specific Gravity. By S. L. Penfield. *Am. J. Sci.*, **50**, 446–448. — A form of apparatus is described for separating, by means of Retger's mixture ($AgNO_3$: $TlNO_3 = 1 : 1$; sp. gr. = 4.5), the heavy constituents of a mineral mixture. It consists of a glass tube whose lower end is somewhat narrowed and ground both inside and out, whereby it may be closed from within by a ground stopper at the end of a rod, and at the same time itself close a small, cup-shaped

vessel for collecting the heavy particles. The liquid and mineral mixture is first introduced into the tube and the heavy constituents allowed to collect in the lower vessel, which, when the stopper has been inserted, is removed and its contents analyzed. The liquid is then diluted and a second separation effected in the same way. — For liquids having a specific gravity greater than 4.5 the author suggests the use of mixtures of silver nitrate and thallium nitrate in the proportions 3 : 4, 2 : 4, 1 : 4, respectively, the last having a specific gravity greater than 4.85 and fusing at about 200° C. Pure thallium nitrate, which fuses at about 250° C., with a sp. gr. of 4.94, may also be used.

Inorganic Chemistry.

H. P. Talbot, Abstracter.

Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reductor. By Andrew A. Blair and J. Edward Whitfield. *J. Am. Chem. Soc.*, **17**, 747–760. — The investigation of the composition of ammonium phosphomolybdate, and the action of zinc upon the molybdic acid contained in it, was carried on as a part of the work of the sub-committee on methods of the International Steel Standards Committee. Ten samples of the phosphomolybdate were prepared, including precipitations from solutions containing ferric nitrate, and from solutions of ammonium molybdate alone. These preparations were washed with water containing varying amounts of nitric acid, and were dried under diverse conditions as regards temperature and time. The dry salt is hygroscopic, and was preserved in glass-stoppered tubes over caustic potash. The phosphoric acid was determined by the addition of magnesia mixture to the ammoniacal solution, re-solution of this precipitate in hydrochloric acid, precipitation of the molybdenum by sulphuretted hydrogen, the re-precipitation of the ammonium-magnesium phosphate, and ignition. The molybdic acid was determined by precipitation with lead acetate, filtration on a Gooch filter, drying at 120° C., and weighing as lead phosphate and molybdate. The ammonia was liberated by distillation with potassium hydroxide, absorption in hydrochloric acid, and ultimate separation as the double platinum salt. The determination of the water offered unexpected difficulties, and was finally achieved by heating in a combustion tube to 250° C. and absorption of the liberated water by calcium chloride. It was shown that no ammonia was liberated during the heating. From the analyses of the ten samples it appears that the average ratio of the phosphorus to 100 of molybdic acid was 1.7946, the extremes being 1.778 and 1.810. The percentages of water varied from 0.71 to 5.02 (in a single instance), the average being about 1.77 per cent., while the ammonia (calculated as $(NH_4)_2O$) varied from 2.64 to 3.39. The variations in the former were probably due to the varying conditions under which the drying occurred, and in the latter to the removal of the ammonia by nitric acid in the wash water. The authors are prepared to adopt as a result of these analyses, "without hesitation," the theoretical ratio 1.794 as the true proportion of phosphorus to molybdic acid in the yellow precipitate. They could not confirm the statement of Hundeshagen (*Chem. News*, **60**, 168) that ammonium phosphomolybdate washed with dilute nitric acid and dried in a desiccator over calcium chloride and potassium hydroxide has the composition $12MoO_3$, P_2O_5, $3(NH_4)_2O$, $4HNO_3$, $2H_2O$. — To test the action of zinc, the phosphomolybdate was dissolved in ammonia, the solution acidulated with sulphuric acid and passed through a special form

of reductor, for a description of which reference must be made to the original article. The reductor was rinsed out with sulphuric acid. The proper time of passage through the reductor was found to be about two minutes, for a hot solution of about 100 cc. in volume for each two tenths of a gram of phosphomolybdate. It was noted that when the same solution was repeatedly passed through the reductor that on the third passage a green oxide of molybdenum was deposited on the zinc. This is soluble in sulphuric acid. It has been assumed by different authorities that the molybdate is reduced by zinc to Mo_2O_3, or $Mo_{12}O_{19}$. The authors conclude that the reduction does not go as far as $Mo_{12}O_{19}$, but rather to $Mo_{24}O_{37}$. In order to determine whether the methods in general use would yield results agreeing with this assumption, portions of the same sample of phosphomolybdate were sent to six different chemists. The average of the results showed 91.68 per cent. of molybdic acid (extremes 90.74 and 93.05), while the gravimetric determination indicated 91.96 per cent. — The authors also examined the yellow precipitate which forms in molybdate solutions, and found it to contain 90.43 per cent. molybdic acid and 9.61 per cent. water, no phosphoric acid, and only traces of ammonia. They conclude that it is caused by the presence of an excess of ammonium nitrate, and recommend the following as a useful method for the preparation of a stable molybdate solution: Mix 100 grams of molybdic acid with 400 cc. of cold, distilled water, and add 80 cc. of ammonia (0.91 sp. gr.); filter, and pour the solution into a mixture of 300 cc. of nitric acid (1.42 sp. gr.) and 700 cc. of water.

The Ferrates. By Claude A. O. Rosell. *J. Am. Chem. Soc.*, 17, 760–769. — The author claims to have obtained sodium ferrate in solution by fusion of ferric oxide and sodium dioxide, and disintegration of the resulting mass with ice water. All attempts to form the iron dioxide from the sodium ferrate or barium ferrate were unsuccessful. Moist barium ferrate was found to be decomposed by all soluble acids, even carbonic acid; the dry salt is more resistant. Carbonic acid forms barium carbonate and ferric hydrate. Barium ferrate is not decomposed by alkaline salts, except by sulphates, which throw down barium sulphate and ferric hydrate. It appears that the supposed formation of thioferrates when sulphuretted hydrogen is passed into solutions of sodium ferrate is in reality a reduction of the ferrates, leaving the green color due to the manganates present. The sodium ferrate was prepared in quantity by passing chlorine through a mixture of ferric hydrate and sodium hydrate. An account of earlier researches on the ferrates and a bibliography are appended. The article leaves much to be desired as regards clear and definite statements.

On the Possibility of the Occurrence of Hydrogen and Methane in the Atmosphere. By Francis C. Phillips. *J. Am. Chem. Soc.*, 17, 801–809. *Am. Gas Light J.*, 63, 647–649. — The author considers that considerable quantities of the gas evolved in early stages of decay of organic remains must have escaped into the atmosphere before the burial of such remains under sedimentary deposits sufficiently compact to preclude the possibility of diffusion, whether it is assumed that the decomposition took place at low temperatures, or at a gentle heat. Experiments show that if seaweed be allowed to decay under water, that the gas evolved during the first ten days is composed chiefly of carbonic acid and hydrogen, while that subsequently given off consists of methane. Gases from shallow swamp waters include carbon dioxide, nitrogen, and methane; those from deeper waters contain

also hydrogen. In regions where natural gas is found, gas bubbles are easily produced by disturbing the sediments at the bottoms of ponds or streams, even when no decay is in progress. This gas, the author believes, comes by slow diffusion from great depths, and escapes into the atmosphere. One sample was found to consist of methane, 93.06 per cent.; nitrogen, 6.70 per cent.; and carbon dioxide, 0.24 per cent. Arguments are offered to show that hydrogen or methane would pass to the outer limits of the earth's atmosphere and remain there. Experiments made on Mount Washington, with palladium chloride, to establish the existence of hydrogen in the atmosphere at that altitude, yielded negative results. The author concludes that ozone would tend to remain in the lower strata of the atmosphere apart from the hydrogen; that nitrous acid, if formed, would not attack either hydrogen or the hydrocarbon; and that at the reduced pressure existing at great altitudes no combination between hydrogen and oxygen would probably take place.

Two Definite Carbides of Iron with Chromium (Molybdenum and Tungsten). By JAMES S. DE BENNEVILLE. *J. Am. Chem. Soc.*, **17**, 791–801. — The author has isolated and examined a ferromolybdenumchromium carbide, to which he assigns the symbol $Fe_7(CrMo)_8C_4$, and a ferrotungstenchromium carbide, with the symbol $Fe_7(CrW)_8C_4$. The properties, probable methods of formation and their significance, as well as the analytical procedure, are fully discussed and described in the paper, to which reference must be made.

The Chlorides of Zirconium. By F. P. VENABLE. *J. Am. Chem. Soc.*, **17**, 842–843. — In an earlier paper (*J. Am. Chem. Soc.*, **16**, 460–475) the author stated that a solution of zirconium hydroxide in hydrochloric acid resulted in the formation of zirconium tetrachloride, which could be recrystallized from concentrated acid. An average of ten analyses showed that the substance contained 39.16 per cent. of zirconium, while the calculated percentage for the tetrachloride is 38.99. It has since been found that the substance contains only 35.5 per cent. of chlorine instead of 61.01 per cent. It is probably an oxychloride, possibly possessing the symbol $Zr_8(OH)_5Cl_7.5H_2O$.

Tellurium. Its Separation from Copper Residues, with Notes on Some New Reactions. By CABELL WHITEHEAD. *J. Am. Chem. Soc.*, **17**, 849–855. — It is doubtful if any copper now produced is free from tellurium, with the possible exception of the native copper of Lake Superior. The average amount present is not far from 0.04 per cent. The copper ores of the West are smelted with gold or silver bearing ores, and these mattes are Bessemerized and the copper sent East to be refined by electrolysis, by which process the impurities are separated in the metallic state or as oxides, or basic salts in the form of a slime. This is treated with boiling 20 per cent. sulphuric acid in an air current, and silver sulphate is added, which causes the copper to pass into solution, and this is washed out of the slime, which now consists of gold, silver, and tellurium, and of lead sulphate. The lead is volatilized, and the remaining bullion melted into bars, which are subsequently dissolved in hot sulphuric acid. The tellurium separates on cooling as tellurous oxide with the gold residue; the silver passes into solution and is recovered. The tellurous oxide and gold are once more treated with hot sulphuric acid, which leaves only the gold. This is purified by fluxing with borax and nitre. The tellurium may be separated from its solution, after re-

moval of the remaining traces of silver as chloride, either by precipitation by copper, or by sulphurous acid; the former method seems to be preferable. Copper telluride is precipitated, from which the copper is removed by oxidation and solution in sulphuric acid. The tellurium is next converted into sodium telluride by fusion with sodium carbonate and charcoal, and the metal is precipitated as a gray powder, by passing a current of air through the aqueous solution. The metal is treated with hydrochloric acid, and subsequently with potassium cyanide solution. The dried metal is finally fused. It contains traces of impurities, chiefly gold, and may be purified by distillation in hydrogen. — The tellurium is largely precipitated by ammonium salts from solutions of sodium telluride according to the equation $Na_2TeO_3 + 2NH_4Cl = 2NaCl + TeO_2 + 2NH_3 + H_2O$. A small amount of the metal remains in solution, but is thrown down by sulphurous acid. It is proposed to examine this very carefully with regard to the possible compound nature of tellurium. Hydrogen telluride was found to precipitate telurium and tellurides from a solution of tellurium chloride slightly acid with hydrochloric acid. — Tellurium when heated with aluminum unites with the latter with explosive violence to form a chocolate colored compound Al_2Te_3. This body is quickly decomposed by water as follows: $Al_2Te_3 + 3H_2O = Al_2O_3 + 3H_2Te$. This is exactly comparable with the behavior of the sulphide. The telluride is not acted upon by water. — Tellurium is easily deposited by the electric current, but not in the reguline state. It can be separated from copper in a potassium cyanide solution containing 3 grams of cyanide for each gram of copper.

Reactions between Copper and Concentrated Sulphuric Acid. By Charles Baskerville. *J. Am. Chem. Soc.*, **17**, 904–912. — The author assumes that the action of concentrated sulphuric acid upon copper may be represented by two primary reactions: (1) $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$, and (2) $5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O$; and two secondary reactions: (1) $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + H_2O$, and (2) $CuS + 2H_2SO_4 = CuSO_4 + S + SO_2 + 2H_2O$. The experiments were carried on in an atmosphere of carbon dioxide and at temperatures ranging from 0° to 270° C. At high temperatures only the first primary reaction takes place, but at lower temperatures both occur, and on prolonged contact the secondary reactions appear. The black residue was shown to consist of cuprous sulphide. In one instance only, in which the air was not expelled from the flask, an oxysulphide, $CuO.2Cu_2S$ was found. Compare Pickering, *J. Chem. Soc.*, **1878**, 112.

On Silicides of Iron. By G. de Chalmot. *J. Am. Chem. Soc.*, **17**, 923–924. — Upon subjecting mixtures of iron filings, charcoal, and sand to the temperature of the electric furnace a silicide of iron containing 23 to 27 per cent. of silicon was obtained. It was white, brittle, and crystalline, and corresponded in composition to the compound Fe_3Si_2. It is only very slowly attacked by aqua regia, and then only to remove iron. It is decomposed by hydrofluoric acid, or by fusion with sodium carbonate and potassium nitrate.

On the Use of Organic Bases in the Preparation of Barium and Calcium Ferrocyanides. By Percy H. Walker. *J. Am. Chem. Soc.*, **17**, 927–931. — The preparation of barium ferrocyanide from the corresponding potassium compound is made difficult by its tendency to form

double ferrocyanides. A similar difficulty is not met with if a suitable organic base is brought into the process. Strychnine ferrocyanide is easily prepared, and from this ammonium ferrocyanide, from which the ammonium may be displaced by boiling with barium hydroxide. Dimethylaniline ferrocyanide may also be formed, which on shaking with barium hydroxide yields the barium salt. The corresponding reaction occurs when calcium hydroxide is used. Dimethylaniline ferrocyanide has the symbol $[C_6H_5N(CH_3)_2H]_2H_2Fe(CN)_6$, and is a white crystalline salt, somewhat soluble in water. Barium ferrocyanide has the symbol $Ba_2Fe(CN)_6,6H_2O$. The crystals are oblique rectangular prisms of the monoclinic system, unaltered in the air, and lose eleven twelfths of their water at 40° C., but retain the residue to the point of decomposition. They are soluble in about 260 parts water at 18° C. — The author suggests that a separation of iron and aluminum may be possible through the use of the strychnine ferrocyanide.

On the Combination of Anhydrous Ammonia and Aluminium Chloride. By J. M. Stillman and Minnie B. Yoder. *Am. Chem. J.*, 17, 748–753. — The aluminum chloride was prepared by heating aluminum foil in a current of dry chlorine and subsequent re-sublimation in the same tube. The chloride was subjected to the action of ammonia either in the same tube or after transfer to a U tube, which was cooled by immersion in water. The dry ammonia, mixed with some air, was at first passed slowly over the chloride, and finally pure ammonia. At the end of twenty-four hours the process was complete, and a light white powder resulted which smelled of ammonia, was non-deliquescent, but decomposed by water. An analysis shows that the composition approximates that of $AlCl_3.6NH_3$, but the amount of ammonia is about 2 per cent. too low. By passing dry air over this compound heated to temperatures between 0° and 100°, a body results which, in its percentage of aluminum and chlorine, approximates the compound $AlCl_3.5NH_3$, but contains from 7 to 15 per cent. less ammonia. Some drops of water were noticed in the tube when the air current was interrupted, and the temperature of the bath maintained at 100°, and at 200° water and ammonium chloride were detected. The authors assume that some of the hydrogen of the ammonia is oxidized to water, that the aluminum is changed to oxide, and that ammonium chloride is formed. They assume that this reaction takes place in some degree during the formation of the original compound, which would explain the deficiency in ammonia noted. Unfortunately, experimental confirmation is not given. The partially oxidized compound was heated to 240° in dry hydrogen, and was changed into a body approximating $AlCl_3.2NH_3$. It is proposed to continue the same line of experimentation with other anhydrous chlorides. (Compare also the abstract, this *Quarterly*, page 314).

On the Existence of the Sulphoxyantimonates. By LeRoy W. McCay. *Am. Chem. J.*, 17, 770–778. — The author has repeated the experimental work of Rammelsberg (*Ann. der Phys. Pogg.*, 52, 193) with the hope that thereby some light might be thrown upon the action of sulphuretted hydrogen upon solutions of antimonic acids, whereby salts of sulphoxyantimonic acid are possibly formed. About 64 grams of antimony pentasulphide were treated with 46 grams of potassium hydroxide dissolved in 250 cc. of water. The flask was violently shaken and allowed to stand twenty-four hours; the potassium metantimonate was removed by filtration, and the reddish filtrate evaporated on the water bath until crystallization just began,

and then allowed to cool slowly. Straw yellow crystals of some size separated, which were dried in a Gooch crucible, pressed between filter paper, and finally dried in a vacuum over lime. The analyses correspond to the composition, $K_2HSbO_2.S_2 + 2H_2O$. It might be considered to be either a double salt, a pyrosulphoxy salt, or as a secondary potassium orthodisulphoxyantimoniate. The first is improbable, and, while there is no proof that it is not a pyrosulphoxy salt, the author thinks it more logical to class it as the latter ortho compound, with which it seems to correspond in its behavior. It loses four fifths of its water at 140°–150° (probably water of crystallization), and the remainder (probably water of constitution) at 250°–260°. The hydrates of the alkaline earths produce in its solution white, crystalline precipitates; silver nitrate produces a black, copper sulphate a dark red, and lead acetate a cherry red precipitate, the last two becoming black on standing. The precipitates do not appear to be sulphoxy compounds. On the addition of a little acetic acid the liquid becomes orange, and a little sulphuretted hydrogen is evolved, which, if not allowed to escape, is again absorbed. Hydrochloric acid throws out a mixture of antimony pentasulphide and trisulphide, free sulphur, antimony pentoxide and trioxide, while some of the last two remain in solution. A small amount of sulphuretted hydrogen is also evolved. The following may represent the reaction on the addition of an acid: $8H_3SbO_2S_2 + 12H_2O = Sb_2S_5 + 2Sb_2S_3 + 5S + H_3SbO_4 + H_3SbO_3 + 21H_2O$.

H. Fay, Abstracter.

On the Ammonium-Cuprous Double Halogen Salts. By H. L. Wells and E. B. Hurlburt. *Am. J. Sci.*, 50, 390–393. — Deherain described three double chlorides, $4NH_4Cl.Cu_2Cl_2.H_2O$, $2NH_4Cl.Cu_2Cl_2$, and $NH_4Cl.Cu_2Cl_2$. The authors were able to obtain the first of these salts without the molecule of water which corresponds to Mitscherlich's potassium salt, $4KCl.Cu_2Cl_2$. This salt crystallizes well, but is readily oxidized on standing. The other chloride obtained, $4NH_4Cl.3Cu_2Cl_2$, crystallizes in brilliant dodecahedrons. Attempts to make the second salt of Deherain failed, but, as the corresponding bromide is easily prepared, its existence seems possible. Deherain's third salt could not be made, and the authors think its existence doubtful. Two bromides were prepared corresponding to the formulæ, $4NH_4Br.Cu_2Br_2$ and $2NH_4Br.Cu_2Br_2$. Only one iodide was obtained, $2NH_4I.Cu_2I_2$, which corresponds to the description of a salt made by Saglier, to which he assigned the formula, $NH_4I.Cu_2I_2.H_2O$. These salts were prepared by bringing together the ammonium and cuprous halogen salts with the corresponding acids in presence of copper wire.

The Reduction of Selenic Acid by Hydrochloric Acid. By F. A. Gooch and P. S. Evans. *Am. J. Sci.*, 50, 400–402. — This paper presents a study of the conditions which are most favorable for the complete and rapid reduction of selenic acid by hydrochloric acid. It was found that so long as the volume of the hydrochloric acid (sp. gr. 1.20) does not exceed 10 per cent. of the entire liquid no chlorine is evolved, and that only when the percentage of this acid rises as high as thirty does the chlorine evolved during five minutes' boiling approach the theoretical yield. Good results may be expected when the mixture, containing one third of its volume of concentrated hydrochloric acid at the beginning, is boiled until all chlorine is expelled, care being taken that the volume of the liquid shall not become less than two

thirds of the original volume. If the hydrochloric acid solution be allowed to boil down to "half strength acid," selenium appears in the receiver. The iodine liberated in the absorption apparatus is determined by standard sodium thiosulphate.

The Reduction of Selenic Acid by Potassium Bromide in Acid Solution. By F. A. Gooch and W. S. Scoville. *Am. J. Sci.*, 50, 402–404. — In a previous paper it has been shown that potassium bromide may be used as a reducing agent in presence of acid to effect the reduction of arsenic and telluric acids. This paper gives the precautions necessary for the reduction of selenic acid by means of potassium bromide in acid solution. The applicability of the reaction to quantitative work depends upon the proportions of the reagents used. The quantities which were found to give the best results were 60 cc. initial volume, containing 20 cc. "one half strength sulphuric acid," with one gram potassium bromide to 0.25 gram of selenic acid. After all bromine is expelled the liquid becomes clear, but on further boiling it is again colored from the decomposition of the excess of potassium bromide. The heating should be discontinued when the color reappears, and the volume of liquid should not be reduced below 35 cc. Under these conditions the reduction is almost theoretically exact. The iodine is titrated with sodium thiosulphate.

Analytical Chemistry.

H. P. Talbot, Abstracter.

Estimation of Sulphur in Pyrites. By G. Lunge. *J. Am. Chem. Soc.*, 17, 772–775. — This article continues the discussion between the author and Mr. T. S. Gladding concerning the details of the procedure for the determination of sulphur in pyrites (compare this *Quart.*, pages 184 and 187). The paper presents no additional experimental data, and is mainly devoted to criticism of Gladding's interpretation and representation of the author's earlier statements, and reaffirms these statements without exception.

The Estimation of Sulphur in Refined Copper. By G. L. Heath. *J. Am. Chem. Soc.*, 17, 814–822. — The author regards the methods of Fresenius and Hampe as inapplicable to refined copper, and while the procedure proposed by Phillips (that of solution in nitric or nitro-hydrochloric acid, and precipitation from an hydrochloric acid solution with barium chloride) is more satisfactory, it does not take into account the possible solvent action of cupric chloride and hydrochloric acid upon the barium sulphate. The experiments made by the author show that if the total volume of the solution does not exceed 100 cc. the barium sulphate is completely precipitated even in liquids containing $3\frac{1}{2}$ per cent. by volume of hydrochloric acid (sp. gr. 1.20). In the presence of $2\frac{1}{2}$ grams of copper and the same amount of acid, in a volume of 350 cc., the precipitation is retarded, but is complete at the end of 72 hours, except with very small amounts of sulphur; but when the amount of copper is increased to 10 grams the solubility of the barium sulphate is considerable. Results of experiments are also presented to show that the sulphate is appreciably soluble in large volumes (700 cc.) of dilute acid without the presence of the copper salt. The direct precipitation is sufficiently accurate for mattes and crude copper, but for refined copper the following

procedure is recommended: The copper (usually 10 grams) is dissolved in 60 cc. of nitric acid (sp. gr. 1.42) and 15 cc. of hydrochloric acid (sp. gr. 1.2), over an alcohol flame. The hydrochloric acid is removed by repeated evaporation with nitric acid, the slightly acid solution filtered, diluted to at least 600 cc., and introduced into an Edison incandescent lamp circuit. The negative electrode should measure about 20 square inches, and the current from two sixteen candle power lamps (parallel) suffices to deposit the copper in one night. The sulphuric acid is precipitated from the liquid, now free from copper, after removal of the nitric acid by evaporation with hydrochloric acid. Sodium carbonate is added in small amount to prevent loss of sulphuric acid, and blank analyses are always necessary. If lead be present, it is mainly precipitated by the current, but if its presence on any of the filters is suspected they must be boiled with sodium carbonate solution.

Acidimetric Estimation of Vegetable Alkaloids. A Study of Indicators. By Lyman F. Kebler. *J. Am. Chem. Soc.*, **17**, 822–831. *J. Franklin Inst.*, **141**, 141–147. — The paper presents the results obtained from the use of five indicators for the titration of alkaloids, great care being taken to insure accuracy. An extract of Brazil wood was prepared by boiling 3 grams of the wood with 10 cc. of water, after which it was cooled and filtered. Of this solution three drops were used in titration, and the end-point was considered to be the change from yellow to onion-red. Cochineal and litmus were prepared according to the directions in Sutton's "Volumetric Analysis," 6th edition. Five drops of cochineal and ten drops of litmus were used. The end-point chosen with the former was the change from yellow to bluish red, with the latter from red to onion-red. The methyl orange solution contained one gram per liter; that of hæmatoxylin one gram in 100 cc. of strong alcohol, and the end-points were red to straw-yellow and yellow to brown-orange, respectively. Three drops of the hæmatoxylin and five drops of the methyl orange solution were used. With normal solutions of sulphuric acid and potassium hydrate the author could detect no difference in sensitiveness of "most of the indicators." The titration of pure alkaloids was conducted as follows: If they are soluble in alcohol, two grams were dissolved in that solvent and the volume finally brought to 100 cc. Of this solution 10 cc. were taken, the requisite amount of indicator solution added, and then a slight excess of decinormal acid. After agitation and the lapse of a few minutes, the sides of the beaker were well washed down with water (about 40 cc.), and the excess of acid determined by titration with centinormal alkali. If the alkaloid examined was not freely soluble in alcohol, the two grams of the substance were mixed with 75 cc. of the decinormal acid, and warmed on the water bath with some shaking until the alkaloid had dissolved. When cold, the solution was made up to 100 cc., and 10 cc. measured off for examination. After the addition of the indicator, and dilution to 50 cc., the excess of acid was determined by titration with the centinormal alkali. This procedure yields satisfactory results as applied both to pure and crude alkaloids. For the extraction of the alkaloid from its natural sources the following procedure is given: About 10 grams of the drug are shaken with 25 grams of chloroform and 75 grams of ether, then 10 grams of 10 per cent. ammonia water are added, and the mixture is shaken at intervals for an hour. On the further addition of 5 grams of the ammonia, the powder collects together and the liquid will clear. Of the liquid 50 grams are taken and (1) placed in a beaker, the solvent evaporated on the water bath, 10 cc. of

ether added and again evaporated, the residue dissolved in alcohol and titrated as above, or (2) placed in a separatory funnel, treated with 20 cc. of acidulated water (the operation being twice repeated), and the aqueous solution separated, and made alkaline in another separatory funnel with ammonia water, and shaken with three portions (20 cc., 15 cc., and 15 cc.) of a mixture of three parts by volume of chloroform and one part ether. This mixture is collected in a tared beaker, the varnishlike residue twice treated with 8 cc. of ether, and evaporated on a water bath, and dried to constant weight. This is subsequently dissolved in alcohol and titrated as above. The results are slightly lower than by Keller's process. — It appears that methyl orange is not reliable as an indicator in these processes, nor is litmus, if prepared according to Sutton. Hæmatoxylin yields the most satisfactory results, and Brazil wood follows in order, while cochineal can also be relied upon. The paper is accompanied by a list of references to the "more valuable literature" on indicators for the last ten years.

On the Analysis of Alloys of Lead, Tin, Antimony, and Arsenic. By LAUNCELOT ANDREWS. *J. Am. Chem. Soc.*, 17, 869–873. — The attempted volatilization of the tin and antimony as chlorides, or by treatment with bromine and hydrochloric acid, was unsuccessful. The antimony, tin, and arsenic were completely separated from the lead by heating to 210° C. in a current of hydrochloric acid gas which had passed through nitric acid (1.50 sp. gr.). The lead remains as pure chloride; the other metals were separated in the distillate by Gooch and Phelps' (*Ztschr. Anal. Chem.*, 7, 123), and Carnot's method (*Ztschr. Anal. Chem*, 88, 650). It is noted that in the latter method the solution should be boiled rapidly until one fourth is boiled away, and that the oxalic acid must be in excess as regards the thiosulphate. As a second method for the separation the following was found useful. The turnings of the alloy are boiled with hydrochloric acid (sp. gr. 1.10) and potassium iodide. The antimony remains undissolved, and may be removed by filtration on a Gooch filter, washed free from lead iodide, and converted to sulphide by heating with sulphur in a current of carbonic acid. The results are satisfactory. The author recommends the use of an ordinary Argand burner, with chimney, for operations where constant and easily regulated temperature is required.

The Determination of Graphite in Pig Iron. By P. W. SHIMER. *J. Am. Chem. Soc.*, 17, 873–876. — The author finds that the residual carbon left after treating an iron with hydrochloric acid contains not only the graphite, but also titanium carbide, while the residue from nitric acid is graphitic carbon only. In a sample of iron containing 3.334 per cent. total carbon, the graphite by nitric acid was 3.206 per cent.; by hydrochloric acid, 3.327 per cent.; indicating in the former case, 0.128 per cent. combined carbon, and in the latter case, 0.007 per cent. Gentle boiling for an hour with nitric acid (sp. gr. 1.2) did not cause oxidation of the graphite in the sample examined. Since the crystals of titanium carbide can be seen distributed through the mass of the iron, and since this carbon so combined does not probably influence the hardness to any extent, it is suggested that it may be advisable to determine not alone the total carbon and the graphitic residue from nitric acid, but also the residue from hydrochloric acid, and from these to determine the amount of carbon as titanium carbide, and of carbon combined with iron and manganese.

On the Volumetric Determination of Titanic Acid and Iron in Ores. By H. L. Wells and W. L. Mitchell. *J. Am. Chem. Soc.*, 17, 878–883. — The ore (10 grams) is dissolved in 100 cc. of concentrated hydrochloric acid by heating for several hours, with renewal of the acid. When no further action is apparent, 50 cc. of equal parts of sulphuric acid and water are added, and the hydrochloric acid is expelled by evaporation. After dilution and solution of the sulphates, the liquid is filtered and any suspicious residue brought into solution by fusion with potassium disulphate. Aliquot parts of the solution of the ore are placed in Erlenmeyer flasks; the iron in two of them is reduced by sulphuretted hydrogen, and titrated with potassium permanganate. To other portions 25 cc. of concentrated sulphuric acid are added, and the iron and titanium reduced at a boiling temperature by a rod of zinc, and cooled in an atmosphere of carbonic acid. The zinc is removed, and the iron and titanium titrated with potassium permanganate, the titanium being estimated from the two titrations by dividing the factor for metallic iron by 0.7. It is necessary to use great care to prevent the oxidation of the reduced titanium compound by admission of atmospheric oxygen. The results obtained were not in a high degree accurate, but the authors consider them more reliable than those ordinarily resulting from gravimetric determinations.

The Evolution Method for the Determination of Sulphur in White Cast Iron. By Francis C. Phillips. *J. Am. Chem. Soc.*, 17, 891–900. — In an exhaustive paper the author gives an account of a series of experiments which show that when an iron is treated with hydrochloric acid in the ordinary procedure, a portion only of the sulphur is evolved as sulphuretted hydrogen, while sulphur may be found in the form of organic sulphur compounds in the oily drops which collect in the flask, and which also remain with the ferrous chloride solution, and are even found in the insoluble residue. These compounds are probably of the character of organic sulphides or sulphydrates, and resist oxidation to sulphuric acid. The author recommends that the decomposition of the iron by hydrochloric acid (sp. gr. 1.12) take place in a flask in an atmosphere of carbonic acid. The escaping gas is led through a porcelain tube heated to redness, containing a roll of platinum foil. The delivery tube is so arranged that any oil that falls from it drops upon the platinum foil, and the boiling is continued until the oily drops are all driven over, which may require two hours. The gases pass through bromine in hydrochloric acid, and then to the bottom of an eight-liter bottle containing some of the bromine solution. The latter precaution is essential for the complete condensation of the sulphuric acid. The results by this method are concordant with those obtained by Blair's aqua regia method.

On the Volumetric Determination of Lead. By Allerton S. Cushman and J. Hayes-Campbell. *J. Am. Chem. Soc.*, 17, 901–904. — The authors propose a modification of the Schwartz method (*Dingl. poly. J.*, 169, 284) as follows: The ore is decomposed by nitric and sulphuric acids, the former expelled, and the lead sulphate washed by decantation. The sulphate is then dissolved in ammonium acetate solution, and an excess of standard potassium bichromate solution is added, the lead chromate filtered off and washed with ammonium acetate solution, and the excess of the bichromate is determined in the filtrate by titration with a standard solution of ferrous ammonium sulphate. If no bismuth or antimony be present, the ore can be di-

rectly dissolved in nitric acid, neutralized with ammonia, and acetic acid added in slight excess. The results obtained were slightly low, but represent about 99.6 per cent. of the true value.

On the Estimation of Phosphoric Acid by Titration of the Ammonium Phosphomolybdate Precipitate with Standard Alkali. By B. W. KILGORE. *J. Am. Chem. Soc.*, 17, 950–968. — As the result of a long series of experiments described in the paper the following procedure is recommended. Two grams of the substance are taken for analysis. If it is of an organic nature it is evaporated with 5 cc. of magnesium nitrate solution, ignited, and dissolved in hydrochloric acid; ordinary phosphates or fertilizers are dissolved in 30 cc. of concentrated nitric acid, with a small quantity of hydrochloric acid, or in 30 cc. concentrated hydrochloric acid, with the addition of potassium chlorate; phosphates containing considerable iron are dissolved in 15 to 30 cc. strong hydrochloric acid, and 5 to 10 cc. of nitric acid. The solution is made up to 200 cc., and 20 cc. are measured off if the percentages are above five, or 40 cc. if below five, and 5 or 10 cc. of nitric acid, according to the method of solution. Ammonia is then added until precipitation begins, the solution is diluted to 75 or 100 cc., digested in a water bath at 60° to 65° C., and precipitated with a filtered molybdate solution, avoiding a large excess. After standing in the bath six minutes the solution is filtered as quickly as possible on a three-inch Hirsch funnel, or a Gooch crucible with paper disks. The former is strongly recommended. The precipitate is washed twice by decantation with dilute nitric acid, once by decantation with a 3 per cent. potassium or ammonium nitrate solution, and finally on the filter with water until no longer acid. The precipitate and filter are then washed into a beaker, potassium hydroxide is added in excess, and the excess determined by titration with nitric acid. Phenolphthalein is used as an indicator. Solutions containing less than 1 per cent. of phosphoric acid may require eight or ten minutes for precipitation.

Estimation of Phosphoric Acid in Soils by Double Precipitation with Molybdic Solution and Titration of the Ammonium Phosphomolybdate with Standard Alkali. By C. B. WILLIAMS. *J. Am. Chem. Soc.*, 17, 925–927. — The procedure recommended is the following: The soil is digested with hydrochloric acid (sp. gr. 1.115) at 100° C. for ten hours. Extracts are also obtained by digestion with 1 per cent. citric acid and 0.63 per cent. oxalic acid for five hours at laboratory temperature. The organic matter in all the extracts is destroyed by evaporation to very small bulk, after the addition of three times as much concentrated nitric acid as the volume of the solution, or, in the case of the organic extracts, by ignition and repeated addition of nitric acid. After dilution to a convenient volume, portions are measured off corresponding to 18 or 20 grams of soil (or 1 to 2 grams in the case of the hydrochloric acid solution), ammonium nitrate is added in considerable quantity, then an excess of ammonium molybdate at 40° C. After four hours the precipitate is filtered off, washed twice with water, and dissolved in dilute ammonia. Nitric acid is added until precipitation begins, then 10 grams of ammonium nitrate; the whole is digested at 65°, 2 cc. of concentrated nitric acid are added with stirring, it is allowed to stand five minutes, 2 cc. of molybdate solution are added, and after eight minutes it is filtered, washed, and titrated according to the method given in the Methods of the Association of Official Agricultural Chemists for 1895.

The Determination of Phosphoric Acid by the Molybdate-Magnesia Method and by Volumetric Method. By B. W. Kilgore. *J. Am. Chem. Soc.*, **17**, 941–943. The author presents data confirming a previously expressed opinion (*J. Am. Chem. Soc.*, **16**, 793), that the results obtained by chemists in general with the molybdate method are too high, probably due to the precipitation of an excess of magnesia with the magnesium ammonium phosphate. The volumetric method as officially prescribed seems to yield more accurate and closely concordant results in the hands of various chemists, than the molybdate-magnesia method.

The Volumetric Estimation of Manganese. By George Auchy. *J. Am. Chem. Soc.*, 943–947. — The author is of the opinion that Low's method is not always reliable; that the Williams method will generally yield satisfactory results, but should be checked by the use of the Volhard method. The following precautions are suggested in connection with the latter method: The amount of sulphuric acid used to replace the nitric acid should not be so large as to cause bumping. The sulphates should be dissolved in hot water before complete cooling, to avoid the formation of a red residue containing manganese. An excess of zinc oxide is to be avoided, and after each addition of permanganate the flask is shaken until a clear yellow is obtained before further addition takes place. It is also suggested that hydrochloric acid may be introduced to advantage if the solution spatter and bump after sulphuric acid is added. Sal soda may be substituted for the anhydrous sodium carbonate in the preliminary neutralization, but a correction must then be made for permanganate consumed by the sal soda.

An Improvement in the Zinc Reductor for the Determination of Iron or Phosphorus. By A. G. McKenna. *Proc. Eng. Soc. W. Pa.*, **11**, 227–230. — The author recommends the use of amalgamated zinc in the reductor to diminish both the evolution of hydrogen during filtration, and the unnecessary consumption of zinc. A special form of tube is employed for the reductor, which is provided with a stopcock to regulate the flow. A small plug of asbestos is placed above the stopcock, and over this about 300 grams of the amalgamated zinc, prepared by stirring it in a beaker with about 5 grams of mercury and 25 cc. of 5 per cent. sulphuric acid. The reduction of the iron or molybdenum is prompt and complete. The usual care must be taken to avoid the passage of air (with formation of hydrogen peroxide), and to insure complete preliminary washing of the reductor with dilute acid.

Methods in Use in the Laboratory of the Duquesne Steel Works. By J. M. Camp. *Proc. Eng. Soc. W. Pa.*, **11**, 251–265. — The paper presents a concise account of the methods employed in the laboratory named, for the analysis of irons and steels, and in some cases also iron ores, for phosphorus, iron, manganese, silicon, sulphur, nickel, and carbon.

H. Fay, Abstracter.

The Iodide Assay for Copper. By Albert H. Low. *Eng. Min. J.* **59**, 124. — The author makes use of the reaction between copper salts and potassium iodide by which cuprous iodide is precipitated and iodine set free, which can be titrated with sodium thiosulphate. — One gram of the ore is

treated with 10 cc. strong nitric acid and then with hydrochloric acid, and finally heated with sulphuric acid until fumes of sulphur trioxide are given off. The solution is diluted with 40 cc. of water, and lead sulphate is filtered off. The copper is then precipitated by placing in the solution a piece of aluminum, washed with water by decantation, and then redissolved in nitric acid and evaporated to small bulk. The excess of nitric acid is neutralized by boiling with an excess of ammonia, and 6 cc. of glacial acetic acid are added. An excess of potassium iodide is now added, and the liberated iodine is titrated. The sodium thiosulphate is standardized by means of pure copper, and the process is carried out just the same as described for copper matte after the redissolving of the precipitated copper. It is essential that no nitrate of copper or free nitric acid be present when the titration is made. The author claims that the accuracy of the method is equal to that of the electrolytic method.

Magnetic Oxide of Iron in Copper Mattes. By Edward Kellar. *Eng. Min. J.*, **60**, 465. — Ten to twenty grams of the matte are treated with an excess of strong nitric acid and allowed to stand in a warm place. Separated sulphur is oxidized by the addition of some potassium chlorate. The beaker containing the solution is placed on the poles of a horseshoe magnet, and the solution is decanted. By this means the magnetic oxide of iron is kept on the bottom of the beaker, and may be washed free from other substances and dried for analysis.

Contributions to the Chemistry of the Cyanide Process. By E. A. Schneider. *Eng. Min. J.*, **60**, 489. — The reaction between cobalt acetate and potassium cyanate, by which the blue double salt $K_2CO(CNO)_4$ is formed, is made use of for the detection of small quantities of potassium cyanate in potassium cyanide. The cyanide to be tested is dissolved in as little water as possible, and most of the cyanide is precipitated with absolute alcohol. The cyanide now remaining in the filtrate from the above precipitation is decomposed by a current of carbon dioxide, and the potassium carbonate is filtered off. To the filtrate is added the cobalt acetate. The blue color is more intense in concentrated solutions and in presence of alcohol. From 1 to 0.35 parts of potassium cyanate can be detected in 100 parts of potassium cyanide.

Proximate and Technical Analysis.

A. H. Gill, Abstracter.

On the Technical Analysis of Asphalt. By Samuel P. Sadtler. *Am. Gas Light J.*, **63**, 779. *J. Franklin Inst.*, **140**, 383–386. — Instead of extracting with petroleum ether, turpentine, and chloroform, as recommended by Miss Linton (*J. Am. Chem. Soc.*, **16**, 809), which is tedious and involves the use of solvents of variable composition, the samples are extracted with acetone and chloroform. The method is as follows: an asbestos filter is made in a Gooch crucible and dried; upon this is placed about 10 grams fine white sand which has been ignited and dried, a piece of stout platinum wire, and the whole dried to a constant weight at 100°. One to two grams of the asphalt or maltha are mixed with the sand, care being taken not to disturb the asbestos, and the crucible and contents again dried to a constant weight at 100°. The loss is called "moisture and loss at 100° C." The crucible and

contents are placed in an extraction apparatus, consisting of a small percolator held by a perforated cork in a large one connected with the flask holding the solvent and a reflux condenser. Acetone is first used, the extraction being continued until the weight is constant within 1 or 2 milligrams after two hours' extraction. The loss of weight is called "petrolene;" chloroform is next used, the final loss being "total bitumen" (asphaltene). The residue in the crucible is "organic non-bitumen" and mineral matter, and on being ignited the "ash" or "mineral matter" is left. The time of extraction varies with the various asphalts, being about twelve hours with acetone and eight with chloroform. The loss in weight should be taken first after four hours, and then every two hours until the extraction is complete, the crucible and contents being dried at 100° each time.

The Proximate Analysis of Coal. By S. W. Parr. *Am. Eng. R. R. J.*, **39**, 374–5. — *Moisture* is determined by heating one hour in an air bath to 105°–110° C.; *Volatile matter*, by heating fifteen minutes in a porcelain crucible in a furnace similar to Hempel's, with a triple burner. *Ash* is determined by burning the coke found above in a stream of oxygen.

Method of Determining the Specific Gravity of Oils and Other Liquids. Chemistry as applied to Railroads. Second Series. By C. B. Dudley and F. N. Pease. *Am. Eng. R. R. J.*, **39**, 449–451. — Careful directions, with illustrations, are given for the determination of specific gravity by the hydrometer, the Westphal Balance, and the pyknometer.

The Determination of Methane and Hydrogen by Explosion. By Augustus H. Gill and Samuel P. Hunt. *J. Am. Chem. Soc.*, **17**, 986–994. — The authors were struck by the fact that the determination of the constituents of a gaseous mixture by explosion is by no means as accurate as that made by absorption with Hempel's apparatus. Mixtures of methane, hydrogen, and nitrogen were made and analyzed (1) by one explosion with oxygen; (2) by two explosions with oxygen, and (3) by one explosion with air, using necessarily about one third as much gas. It was found that the results obtained by the first method were accurate to less than 0.5 per cent. of the methane and 0.3 per cent of the hydrogen; those by the second method to within 0.2 and 0.3 per cent., respectively; and those by the third to within 0.9 and 7.5 per cent., respectively. They find, also, that pure methane cannot be obtained by heating soda lime with sodium acetate, and that for the accurate determination of hydrogen the Hempel ratio of 1 : 6 for explosive to inert gases must be closely adhered to. They find further that when a mixture of methane and hydrogen is exploded with a quantity of oxygen insufficient for both, but more than sufficient for either, about 60 per cent. of the hydrogen, 25 per cent. of the methane, and 50 per cent. of the oxygen are consumed.

Geological and Mineralogical Chemistry.

W. O. Crosby, Abstracter.

The Constitution of the Silicates. By F. W. Clarke. *Bull. U. S. Geol. Survey, No.* 125, 1–109. — If all of the silicates were salts of a single silicic acid, the problem of their constitution would be relatively simple; but this is not the case. Many silicic acids are theoretically possible, and several

of them have representatives in the mineral kingdom, although the acids themselves, as such, are not known. Their nature must be inferred from their salts, and especially from their ethers, and this side of the problem is the first to be considered. Since silicon is quadrivalent, its ortho acid is necessarily represented by one atom of the element united with four hydroxyl groups, thus $Si(OH)_4$. To this orthosilicic acid the normal silicic ethers and many common minerals correspond. Its normal salts are: $R^{i}_{4}SiO_4$, $R^{ii}_{2}SiO_4$, $R^{iii}_{4}(SiO_4)_3$, $R^{iv}_{4}SiO_4$. Any silicate in which the oxygen atoms outnumber the silicon atoms by more than four to one, as in Al_2SiO_5, must be regarded as a basic salt. By the elimination of water orthosilicic acid may be conceived as yielding, first, metasilicic acid, H_2SiO_3, and, secondly, the anhydride, SiO_2. Corresponding to metasilicic acid many salts are known, but as yet no ethers have certainly been obtained. In like manner, by the elimination of varying proportions of water, are derived three other acids — diorthosilicic, dimetasilicic, and trisilicic — which are also represented among native silicates. If the natural silicates were simple normal salts of the five silicic acids, the problem of their constitution would not be difficult; but the greater number are double salts, and even triple replacements are not uncommon. Furthermore, there are acid and basic salts to be interpreted, and the latter class is shown to offer especially serious difficulties. A hasty glance over the entire field of the natural silicates will show, first, that many of them are most easily interpreted as orthosilicates, and, secondly, that by far the greater number are salts of aluminum. Attention is specially called to the fact that aluminum is now properly regarded as a trivalent metal, and twelve minerals are cited as derivatives from normal aluminum orthosilicate, $Al_4(SiO_4)_3$. Among the orthosilicates of aluminum and other triads, including ferric oxide, are comprised: (1) the nephelite type, in which a single aluminum atom is replaced by three monads; (2) the garnet-biotite type, in which two atoms of aluminum have been replaced partly by univalent and partly by bivalent atoms; (3) the feldspars and scapolites, which are regarded as more or less complex mixtures of orthosilicates and trisilicates; (4) the normal zeolites, which may be regarded as substitution derivatives of the feldspars; (5) the micas and chlorites, which are found to constitute a very complete series of derivatives by substitution from aluminum orthosilicate, replacing in succession one, two, and three of the four atoms of aluminum; (6) the tourmaline group, which is characterized by containing boron, and also by the constant relation of the different types to the micas. Each of these groups is discussed in great detail, with elaborate structural formulæ for all the leading species. In like manner are treated the orthosilicates of dyad bases and tetrad bases. And then follow briefer chapters on the diorthosilicates, and the meta and dimetasilicates. The complexity and detail of this paper are somewhat relieved by the summary in which the formulæ for all the species considered are classified and tabulated.

The Bauxites. A Study of a New Mineralogical Family. By FRANCIS LAUR. *Trans. Am. Inst. Mining Eng.*, **24**, 234–242. — A historical sketch of the discovery and uses of bauxite is followed by the distinction of five varieties based upon composition. It is first noted, however, that a study of all available analyses shows one constant, alumina (Al_2O_3), which varies but little from 68 to 70 per cent., and three variables, water, silica, and ferric oxide, and the sum of the weights of these is constant also at about 27 per

cent. This gives for the centesimal formula of the bauxites 68 to 70 Al_2O_3 + 27 (SiO_2, Fe_2O_3, H_2O) + 4 (sundry accessories). The three variables may replace each other almost indefinitely without changing their total of 27 per cent. The basis or essential compound of bauxite is bihydrate of alumina (hydrargillite) with about 27 per cent. of water, and the proportion of water decreases, in general, with increase of ferric oxide and silica, the alumina playing the part of an acid toward the ferric oxide and of a base toward the silica. The five distinct types are as follows: 1. Hydrargillite (the pure type of bauxite). 2. Pale bauxite (hydrargillite with basic silicate of alumina). 3. Maximal siliceous bauxite (basic silicate of alumina). 4. Red bauxite (hydrargillite with aluminate of iron). 5. Maximal ferruginous bauxite (aluminate of iron). The existence of definite manganiferous, titaniferous, and other varieties is regarded as probable by the author. He calls the bauxites natural lakes, and predicts that all substances capable of uniting with aluminum hydrate may constitute some day, mineralogically, a family of aluminum compounds in the humid way as numerous as the aluminum family in the dry way; and the existence of several distinct hydrates is noted as greatly increasing the possibilities. The author believes that the bauxites originate in the deposition of gelatinous alumina and the combination with this of ferric oxide, etc., to form lakes. In the discussion of this paper by A. E. Hunt numerous analyses are quoted, and he shows that the silica varies inversely as the water of hydration.

The Geological Relations of the Southern Appalachian Bauxite Deposits. By C. Willard Hayes. *Trans. Am. Inst. Mining Eng.*, **24**, 243–254. — This is chiefly a stratigraphic paper, but in discussing the origin of the bauxites of Georgia and Alabama the author advances, as if it were new, the explanation proposed thirty years ago by Dr. T. Sterry Hunt, viz., that the oxidation of pyrite and other metallic sulphides in deep-seated aluminous shales gives rise to various sulphates, including aluminum sulphate and alum, and the reaction of these sulphates with the ubiquitous carbonates ($CaCO_3$) produces either directly or by subsequent oxidation flocculent precipitates of aluminic and ferric hydrates, in which are often subsequently developed during solidification the pisolitic structure so characteristic of both bauxite and limonite.

Iron Ores of East Texas. By W. Kennedy. *Trans. Am. Inst. Mining Eng.*, **24**, 258–288. — The iron ore deposits, which occur in nineteen counties, with an actual area of 1,000 square miles, are referred to the Eocene division of the Tertiary; and the ores, which are all limonites, are classed as nodular, laminated, and conglomerate. A brief historical sketch and a somewhat extended discussion of the geology of the deposits are followed by the chemical analyses. The conglomerate ores, being of little economic interest, are not represented in the analyses. From a study of all the existing analyses, the normal composition of the ores is judged to be as follows: Nodular ores: Fe, 52.77; P, 0.097; S, 0.148; SiO_2, 9.73; ratio, P : Fe, 0.183. Laminated ores: Fe, 45.84; P, 0.114; S, 0.076; SiO_2, 14.91; ratio, P : Fe, 0.248. Numerous analyses classified by counties are next given, followed by analyses of the pig iron produced from the ores. Analyses of the ores and irons of other Southern States are then quoted for comparison, the result being favorable to Texas, as regards both the richness and purity of the ores.

The Phosphates of Tennessee. By Thomas C. Meadows and Lytle Brown. *Trans. Am. Inst. Mining Eng.*, **24**, 582–594. — The phosphate rock forms a thin layer (1 to 4.5 feet) in the Devonian of Middle Tennessee. Twenty determinations of the proportion of bone phosphate in the rock show a variation from 20.40 to 71.92 per cent.

Notes on Magnetite. By William B. Phillips. *Eng. Mining J.*, **60**, 149–150, 176, 196–197. — The author has endeavored to elucidate the questions as to what magnetite really is, how it may be produced, and the influence exerted by the amount of iron as protoxide upon the practical separation over a magnetic concentrator. The chemical constitution and structural formula are first discussed, and the conclusion reached that magnetite (Fe_3O_4) is a ferrous ferrate, as red lead (Pb_3O_4) is a plumbous plumbate. Numerous analyses are then quoted to show the remarkable variations in the ratio of FeO to Fe_2O_3, the extremes being 1 : 0.38 and 1 : 47.02. The protoxide of iron is stated to be non-magnetic, becoming magnetic by partial oxidation, as in the preparation of artificial magnetite from ferrous carbonate, while the sesquioxide, as is well known, becomes magnetic at high temperatures through partial deoxidation. The artificial formation of a magnetic hydrous oxide ($Fe(OH_2)Fe_2O_3$) is noted. The proportion of partially deoxidized iron required for the efficient concentration of hematites is believed to be small, and a possible economy in the magnetization of these ores by producer gas is suggested. The stability of magnetite is seen in the fact that even in an oxidizing blowpipe flame it does not readily take on oxygen and lose its magnetism. A practical standard of magnetism, or means of grading ores for magnetic concentration, is regarded as an important desideratum.

A Further Contribution to Our Knowledge of the Laurentian. By Frank D. Adams. *Am. J. Sci.*, **50**, 58–69. — The author describes the stratigraphy and petrography of the Laurentian series in the district north of Montreal between the Ottawa and St. Lawrence Rivers. The rocks include, besides anorthosites and granites of undoubted igneous origin, and crystalline limestones and quartzites which must be altered sedimentary deposits, extensive areas of gneisses and other foliated and banded rocks whose origin cannot be safely inferred from stratigraphic and petrographic characters. For these a chemical test is proposed, based upon the well-established fact that slates, or the sedimentary rocks of clastic origin which are poorest in alkalies, contain on an average about two thirds of the amount of alkali present in the average granite. Original analyses of five of the Laurentian gneisses are then introduced, and comparison shows that three of these have the composition of slates, while the other two are, in composition, typical granites.

Mineralogical Notes. By Wm. H. Hobbs, with Analyses by Herman Schlundt and Louis Kahlenberg. *Am. J. Sci.*, **50**, 121–128. — 1. *Cerussite with superficial film of galena from near Missoula, Montana.* A complete analysis shows the crystals to be nearly pure cerussite, and the coating of galena, being due to the replacement of CO_3 by S through the agency of H_2S, is a typical *Umhüllungspseudomorphose* after cerussite. 2. *Barite and manganite from the Lucy Mine, Negaunee, Michigan.* The barite was not analyzed. A complete analysis of the manganite crystals agrees closely with the theoretical composition, after deducting between 3 and 4 per cent of Mg, Ca, and Ba carbonates. 3. *Chloritoid from blocks on the south shore of Michigamme Lake, Michigan.* The chloritoid forms large crystals in a phyllitic schist,

which is composed of fine scales of muscovite with large flakes of biotite, and contains besides the chloritoid small amounts of tourmaline, magnetite, and quartz. The last three minerals also occur as inclusions in the chloritoid and vitiate the analysis, which is found to agree quite closely, however, with an analysis by Jackson of masonite from Natick, Rhode Island. 4. *Apatite and essonite in a pegmatite from Canaan, Connecticut.* No analyses were made of these species.

Calaverite from Cripple Creek, Colorado. By W. F. Hillebrand. *Am. J. Sci.*, **50**, 128–131. — The rich telluride ores of Cripple Creek carry, besides the gold, a small amount of silver; and in order to determine whether the metalliferous mineral is calaverite or sylvanite carefully selected samples from three different mines were analyzed. Omitting obvious impurities, the atomic ratio of tellurium to metal was found in each case to be very nearly 2 : 1, as required for both calaverite and sylvanite; but the low percentages of silver (0.90, 1.77, 3.23) refers the mineral at once to the former species, and the interesting fact is noted that calaverite has not heretofore been known to carry less than 3 per cent. of silver.

On the So-called Schneebergite. By A. S. Eakle and W. Muthman. *Am. J. Sci.*, **50**, 244–246. — The object of this investigation was to determine the true nature and validity of this rare species. It had never before been quantitatively analyzed; but qualitative analysis had given antimony and calcium as the principal constituents. The authors found, however, that it contains not even a trace of antimony, but has the composition of a very pure lime-iron garnet (topazolite), with the formula $3CaOFe_2O_33SiO_2$. The physical and pyrognostic characters are shown to accord perfectly with this analysis.

On Two New Meteorites. By E. E. Howell. *Am. J. Sci.*, **50**, 252–254. — These meteorites, which are recent discoveries in Cherokee County, Georgia, and on the El Capitan Mountains, New Mexico, are holosiderites. They were analyzed by H. N. Stokes, of the United States Geological Survey, and found to be entirely normal in composition, containing, respectively, 6.70 and 8.40 per cent. of nickel. The Widmanstätten figures are strongly marked in both meteorites.

The Crystalline Rocks of Missouri. By Erasmus Haworth. *Missouri Geol. Survey, Ann. Rep.*, 1894, **8**, 84–222. — This monograph, which is illustrated by fifteen cuts and thirty plates, is a complete and elaborate account of the granites and porphyries and associated dike rocks of Southeastern Missouri. These rocks have long been of exceptional interest to students of American geology, since they formed an island, or rather an archipelago, in the early Paleozoic sea, as now in the early Paleozoic strata, and their geographic, topographic, and stratigraphic relations to the stratified formations are, therefore, described with some fullness. The good and sufficient reasons for regarding these ancient crystalline rocks as wholly of igneous origin are also carefully noted, and the general conclusion is stated that the porphyries are chiefly effusive (surface flows of lava). The detailed petrographic description of each group is accompanied by a series of original chemical analyses, and analyses of the similar rocks of other regions are quoted for comparison. The dike rocks, which are the newest of the crystallines, are wholly

basic (diabases), the silica ranging from 45.4 to 53.4 per cent. The proportion of iron is above the average, and, what is more exceptional, it is chiefly ferric. The ratio between the lime and soda is normal, and indicates that the feldspars are chiefly labradorite and bytownite. The analyses of the granites and granite-porphyries present no unusual features, except relatively high percentages of soda, due to the large amounts of plagioclase present. The porphyries range from very decidedly acid to comparatively basic varieties — SiO_2, 77.88 to 59.72 per cent.; and like the granites they run high in soda. They are, as is usually the case, slightly more basic than the granites, and richer in alkalies; but the alkalies are in every instance insufficient to make them good keratophyres. The most of the porphyries also contain abnormally high percentages of iron for rocks in which the ferro-magnesian silicates are wanting, the combined oxides aggregating 7 per cent. in two analyses. It is interesting, again, to note that the dike rocks within a few miles of the Mine la Motte lead mines, at which nickel ores have been found in considerable quantity, contain appreciable amounts of nickel, suggesting that the nickel ores may have been derived from the neighboring crystalline rocks.

Geology of the Green Mountains in Massachusetts. By RAPHAEL PUMPELLY, J. E. WOLFF, AND T. NELSON DALE. *Monographs, U. S. Geol. Survey*, **23**, 1–206. — This work contains but little of chemical interest, only two analyses (of albite) being communicated.

Natural Mineral Waters of the United States. By A. C. PEALE. *U. S. Geol. Survey, Ann. Report*, 1892–93, **14**, 49–88. — In this general discussion of our mineral springs the author proposes a chemical classification which is believed to admit of general application. Springs are distinguished, first, as non-thermal or thermal; second, as alkaline, alkaline-saline, saline or acid; third, as sulphated or muriated; fourth (according to the gaseous contents), as non-gaseous, carbonated, sulphureted, azotized, or carbureted; fifth, as sodic, lithic, potassic, calcic, magnesic, chalybeate, or aluminous. The diverse modes of expressing the results of analyses are noted, and the system recommended by the Chemical Society of Washington is approved.

The Laccolitic Mountain Groups of Colorado, Utah, and Arizona. By WHITMAN CROSS. *U. S. Geol. Survey, Ann. Report*, 1892–93, **14**, 157–241. — The general discussion following the detailed descriptions of the laccolites is accompanied by a series of nineteen complete analyses of the rocks, no fewer than sixteen constituents (oxides) having been determined; and these analyses afford a basis for definite conclusions concerning the relations of the composition to the mineralogical and textural developments during the solidification of the magmas.

The Gold-Silver Veins of Ophir, California. By WALDEMAR LINDGREN. *U. S. Geol. Survey, Ann. Report*, 1892–93, **14**, 243–284. — The quartz mines of Ophir are located near the contact of a mass if of granodiorite with amphibolite schists. The lithologic descriptions of these wall rocks and some associated dikes are rendered more complete by thorough chemical analyses. Near the veins the wall rocks are altered to a calcite-sericite aggregate, and other analyses throw light upon the nature and cause of this alteration and the problem as to whether or not the vein contents have been derived from the walls. The conclusion is reached that, while the pyritiferous or so-called

iron belts of the wall rocks are probably a source of local enriching of the veins, the derivation of the largest part of the precious metals must as yet be considered an open question.

Geology of the Catoctin Belt. By Arthur Keith. *U. S. Geol. Survey, Ann. Report*, 1892–3, **14**, 285–395. — In the masterly discussion of the genetic, stratigraphic, and topographic relations of the various formations composing this complex area, chemical considerations play a very minor part, being chiefly limited to analyses of the igneous rocks — granite, quartz-porphyry, andesite, Catoctin schist (an altered diabase), and a single analysis of the great Shenandoah limestone.

The Rocks of the Sierra Nevada. By H. W. Turner. *U. S. Geol. Survey, Ann. Report*, 1892–93, **14**, 435–495. — The descriptions of nearly all the leading types of igneous rocks occurring in the region studied are accompanied by one or several analyses, the aggregate number exceeding fifty; but no attempt is made to compare or discuss the results, or to connect the different rock types as successive phases in the differentiation of a deep-seated magma.

Segregation in Ores and Mattes. By David H. Browne. *School Mines Quart.*, **16**, 297–311. — Analyses representing different parts of the pots of copper-nickel-iron matte from the furnaces at the Copper Cliff Mine near Sudbury, Ontario, show a marked tendency toward a separation of the copper from the nickel and iron, the proportion of copper being greatest in the upper and outer parts of the pots where cooling was most rapid, while the central and sub-central part is richest in nickel and iron. This illustrates the theory of magmatic differentiation based upon Soret's principle, and affords a striking confirmation of the view that the copper-nickel ore deposits of the Sudbury district are of igneous origin, a view to which Bell, Kemp, and others had been led by purely geological studies.

The Elk Garden and Upper Potomac Coal Fields of West Virginia. By Joseph D. Weeks. *Trans. Am. Inst. Mining Eng.*, **24**, 351–364. — The general description of these bituminous coal basins is accompanied by analyses of the coals quoted from the United States Geological Survey and ten hitherto unpublished analyses of the coke produced from the coals.

Graphite Analysis. By S. J. Gormly. *Bull. Missouri Mining Club*, **1**, Part 2, 11–13. — The analysis represents the first and only piece of graphite ever found in Missouri. It is a float specimen, but is supposed to have originated in the Archæan rocks. The analysis gave: C, 38.59; S, 1.63; H_2O, 1.7; tarry matter, 6.99; ash, 51.08. The ash analysis gave: SiO_2, 92.102; Fe_2O_3, 3.542; MgO, 1.098, alkalies, 3.192; = 99.934.

Composition of Cleaned Ores of Southwest Missouri. By H. G. Spencer. *Bull. Missouri Mining Club*, **1**, Part 2, 50–51. — This is the second paper of the series intended to cover every mining camp in Southwest Missouri. Complete analyses are given for ten samples of blende (sphalerite), one sample of chats (impure blende), and three samples of galena.

Occurrence of Tellurium in Oxidized Form Associated with Gold. By Richard Pearce. *Proc. Col. Sci. Soc.*, April 1, 1895. — The hard, compact gold ores of the Ruby Basin in the Black Hills were found, on careful analysis, to contain tellurium, both in the unoxidized or blue ore and the oxidized or red ore, the tellurium in the latter case being presumably in the form of oxide. It was further proved by experiment that in the roasting of gold-silver tellurides only a small proportion of the tellurium escapes by volatilization, the remainder being left in the ore as TeO_2.

The Dyke on the Columbia Vein in Ward District, Boulder County, Colorado. By C. S. Palmer and W. B. Stoddard. *Proc. Col. Sci. Soc.*, October 7, 1895. — The description of the dike, some two hundred feet wide, of felsite porphyrite is followed by a duplicate analysis. The rock is thus shown to be highly altered, but it presents no points of special interest.

On an Occurrence of Copper in Western Idaho. By R. L. Packard. *Am. J. Sci.*, **50**, 298–300. — The copper ore (chiefly bornite) of the Seven Devils Mountains is associated with a granitic rock, which proves, on examination of a thin section, to be a diorite; and this conclusion is confirmed by the chemical analysis, which afforded only 53.98 per cent. SiO_2, and shows a marked predominance of soda over potash.

Effect of the Mutual Replacement of Manganese and Iron on the Optical Properties of Lithiophilite and Triphylite. By S. L. Penfield and J. H. Pratt. *Am. J. Sci.*, **50**, 387–390. — Numerous complete analyses of lithiophilite and triphylite by Penfield and Wells show a transition from essentially $LiMnPO_4$ to the isomorphous $LiFePO_4$. The pure end products are not known, the lithiophilite richest in manganese containing 40.9 per cent. MnO and 4.0 per cent. FeO, and the triphylite richest in iron containing 36.2 per cent. FeO and 9.0 per cent. MnO. The theoretical composition of the pure end products is: Lithiophilite, P_2O_5 : 45.3; MnO : 45.1; Li_2O : 9.6. Triphylite, P_2O_5 : 45.0; FeO : 45.5; Li_2O : 9.5. Hence, if the amount of FeO is known, that of MnO may be told within 1 per cent. by deducting the percentage of FeO from the mean percentage of the bivalent oxides, 45.3. The investigation of the optical characters shows that they undergo a very considerable change, due to the interchange of manganese and iron, which is surprising considering how nearly alike the two elements are in atomic weights. With an increase in iron there is an increase in the indices of refraction, and also the divergence of the optical axes changes rapidly.

Igneous Rocks of Yogo Peak, Montana. By W. H. Weed and L. V. Pirsson. *Am. J. Sci.*, **50**, 467–481. — Yogo Peak is a huge chimney or stock of massive, granular, igneous rocks, a former center of volcanic activity. It is oval in outline, and the rocks show a progressive differentiation along its major axis. The essential minerals are the same throughout, orthoclase and augite; but there is a progressive increase in the ferro-magnesian species toward the western end of the stock. Three rock types — Syenite, Yogoite, and Shonkinite — are distinguished, and the fact that they form a natural series is very clearly brought out in the highly elaborate chemical analyses

made by Dr. W. F. Hillebrand, a chemist whose skill and painstaking accuracy have been of vast service to American petrography. Following is a comparison of the chief rock-making oxides:

	Syenite.	Yogoite.	Shonkinite.
SiO_2	61.65	54.42	48.98
Al_2O_3	15.07	14.28	12.29
Fe_2O_3	2.03	3.32	2.88
FeO	2.25	4.13	5.77
MgO	3.67	6.12	9.19
CaO	4.61	7.72	9.65
Na_2O	4.35	3.44	2.22
K_2O	4.50	4.22	4.96
TiO_2	0.56	0.80	1.44
BaO	0.23	0.32	0.43
P_2O_5	0.33	0.59	0.98

Almost without exception the change is progressive. The silica, alumina, and soda diminish; the iron oxides, lime, and magnesia increase; the potash remains the same or relatively increases. The rarer and less essential oxides (TiO_2, BaO, P_2O_5) show a similar gradation. — Brögger has applied the term "Facies suit" to such a series of rocks originating in the differentiation of an individual mass; and the gradation often exhibited by independent magmatic eruptions in the same region is termed, by way of distinction, a "Rock series." To show the existence of a true rock series in the Yogo Peak district (Little Belt Mountains), analyses, also by Dr. Hillebrand, were made of a quartz syenite porphyry and a minette; and a comparison of the chief oxides for the five types in tabular form shows a remarkably regular gradation. The variations are all along the same line as those shown at Yogo Peak itself; and the gradual fall of silica, alumina, and soda together, with the predominance of potash over soda, may be taken as characteristic of this "petrographical province." The importance of taking account in the classification of rocks, not only of their structure and the *kinds* of minerals they contain, but also of the proportions of the component minerals, is insisted upon; and this is but one of many indications that chemical composition is becoming again, as it was in the early days of geology, an important factor in systematic lithology.

Preliminary Note on a New Alkali Mineral. By Warren M. Foote. *Am. J. Sci.*, 50, 480–481. A qualitative examination shows that the new species Northupite from Borax Lake, California, is a double chloride and carbonate of sodium and magnesium.

The Effusive and Dyke Rocks Near St. John, N. B. By W. D. Matthew. *Trans. N. Y. Acad. Sci.*, **14**, 187–218. — This is a petrographic study. The effusive rocks include quartz porphyry, felsite porphyry, diabase, and feldspar-porphyrite; and the dike rocks consist of diorite-porphyrite, diabase, and augite-porphyrite. A soda granite not included in the author's earlier paper on the platonic rocks of this district is also described. Three analyses are given — one of the soda granite, which is compared with similar occurrences in Minnesota; one of diorite-porphyrite, and one of diabase; but the analyses are not discussed.

A Geological Reconnoissance in Northwest Wyoming. By George H. Eldridge. *U. S. Geol. Surv., Bull.* 119. — This is a systematic account of the general geology of an area of 24,750 square miles in the region of the Big Horn Mountains. The Laramie coals are the chief feature of the section on economic geology, and about forty analyses of the coals are given in tabular form.

The Dyke on the Columbia Vein in Ward District, Boulder County, Colorado. By Charles S. Palmer and William B. Stoddard. *Proc. Col. Sci. Soc., Oct.* 7, 1895. — This dike is a prominent feature in the geology of the region, and of exceptional importance in its relations to the neighboring ore deposits. The rock is a kaolinized and highly silicified felsite porphyrite, containing a large proportion of secondary quartz. An analysis is given, which corroborates the microscopic characters and general appearance of the rock, the chief constituents being silica, alumina, ferric oxide, lime, and water.

Geological Survey of Iowa. *Third Annual Report* (1894). — This volume embraces detailed descriptions of the geology of six counties. Particular attention is given to the economic geology, and under that head are introduced occasional analyses of iron ores, clays, etc.

Geology of New York. By the State Geologist. *Thirteenth Annual Report* (1893), **1**. — In the report on a preliminary examination of the general and economic geology of four townships in St. Lawrence and Jefferson Counties, C. H. Smyth, Jr., discusses at some length the origin of the red hematite of Antwerp and Rossie, and introduces two analyses of the so-called "serpentine gangue" or matrix of the ore to sustain his view that it is an altered granite.

The Classification of the Upper Paleozoic Rocks of Central Kansas. By Charles S. Prosser. *J. Geol.*, **3**, 764–796. — This is a stratigraphic paper; but the author gives, quite incidentally, two analyses, made by Warren Finney, of the limestones of the Chase formation (Permian) to show that they are not highly magnesian, as had been supposed.

Absarokite-Shoshonite-Banakite Series. By J. P. Iddings. *J. Geol*, **3**, 935–959. — In the region of the Yellowstone National Park there are igneous rocks of a peculiar type, which are associated with the normal andesites and basalts of the region, but which differ from them mineralogically and chemically, and deserve a special classification. These rocks occur in a num-

ber of separate localities within this region, where it is apparent that their generic relations are with normal basalts and andesites, and in each locality the varieties having the peculiarities in question are genetically related to one another by differentiation. But all of these peculiar varieties in the region are not closely related to one another, for they are separate offshoots from distinct reservoirs of magma, and were probably produced by similar processes of differentiation. In other words, they are similar rocks that belong to separate but similar classes of rocks. The three classes or types designated by the names in the title are described in detail, and a series of complete analyses is given for each. The analyses are closely studied and compared, and then discussed in their relations to the similar rocks of the adjacent regions and of Norway.

Organic Chemistry.

J. F. Norris, Abstracter.

A New Reagent for Bromine and Iodine. Preliminary Notice Concerning the Halogen Derivatives of the Sulphonamides. By J. H. Kastle. *Am. Chem. J.*, 17, 704–708. — When a solution of parachlorbenzenesulphonamide in caustic soda is treated with bromine water, a yellow crystalline precipitate is obtained which has the formula $C_6H_4ClSO_2NH_2Br_2$ or $C_6H_4ClSO_2NBr_2$. The author promises further work to decide between these two structures. The analogous dichlor-derivative of benzenesulphonamide decomposes metallic bromides and iodides with the formation of metallic chlorides and the corresponding brom- and iodo-derivatives of the amide. When this decomposition was effected in the presence of carbon bisulphide or chloroform, the latter solvents were colored yellow and violet. It was found, with this reagent, that it was possible to recognize 0.00635 milligram of iodine in the presence of 0.36 milligram of bromine. The dichlor-derivative of benzenesulphonamide melts at 70° and is nearly insoluble in hot water. When heated to 170° it decomposes with evolution of chlorine, nitrogen, and hydrochloric acid, and gives almost the theoretical quantity of benzenesulphonchloride.

On Halogen Addition-Products of the Anilides. (Preliminary Paper.) By H. L. Wheeler. *Am. Chem. J.*, 17, 612–619. — When bromine is mixed with dry metanitroacetanilide, the substances combine with evolution of heat, but without giving off hydrobromic acid. When this mixture is heated, torrents of hydrobromic acid are evolved and parabrommetanitroacetanilide is formed. The bromine addition-product was isolated as follows: Metanitroacetanilide was dissolved in nitrobenzene, an excess of bromine added, and the clear solution then precipitated with ligroïn. A heavy, translucent, dark-red oil separated, which was repeatedly treated with ligroïn to remove the excess of bromine. On exposing the oil to the air it immediately solidified to a crystalline mass soluble in chloroform and glacial acetic acid. It can be crystallized from these solvents if free bromine is present. The analysis shows that the compound is a dibrom addition-product of the formula $C_8H_8N_2O_3.Br_2$. Hydrobromic acid is liberated from the compound, with consequent formation of parabrommetanitroacetanilide on heating or on crystallizing it from water. Cold concentrated nitric or sulphuric acid also separates

hydrobromic acid, and at the same time displaces the bromine forming metanitroacetanilide. It is not probable that the addition-product has the structure, $C_6H_4NO_2.NHBr_2.COCH_3$, in which the two bromine atoms are joined to the nitrogen, because methylmetanitroacetanilide, $C_6H_4NO_2.NCH_3.COCH_3$, forms an analogous addition-product which gives off hydrobromic acid readily and forms a bromine substitution-product. In this latter case there is no hydrogen combined with the nitrogen to unite with the bromine to form the acid. The formation of the substitution-product is readily explained if it is assumed that the bromine adds itself to the benzene nucleus, an assumption which is rendered exceedingly probable by the fact that metanitroacetanilide combines with more than two atoms of bromine. This higher addition-product decomposes readily, and was not obtained in a pure condition. Attempts were made to prepare the dibrom addition-product by passing hydrobromic acid gas into a solution of parabrommetanitroacetanilide in a mixture of glacial acetic acid and ethyl acetate. An isomeric addition-product, which has probably the structure of an ammonium salt, was thus obtained. When the anilide was dissolved in acetic acid, and the gas was passed in for a short time, colorless crystals separated, having the composition $(C_8H_7N_2O_3Br)_2HBr$. Both addition-products lose hydrobromic acid when exposed to the air.

Synthesis of Diphenylbiphenyl and its Identification as Benzerythrene. By Arthur A. Noyes and Rolfe M. Ellis. *Am. Chem. J.*, **17**, 620–622. — The purpose of the investigation was to prepare synthetically diphenylbiphenyl, $C_6H_5.C_6H_4.C_6H_4.C_6H_5$, and to determine whether it is one of the products of the action of heat on benzene. Parabrombiphenyl was made as described by Schultz, and treated, in an ethereal solution, with sodium. After the action had continued for two or three days the insoluble residue, which was found to contain the product of the reaction, was first treated with boiling water to remove the excess of sodium bromide, and then with benzene, which dissolved much the larger portion, consisting of a brown flocculent substance which could not be purified. The residue, insoluble in benzene, furnished a sublimate in the form of white crystalline leaflets, which proved to be diphenylbiphenyl by analysis and by a vapor density determination. The yield was 5 per cent. of the theoretical. The substance meets at 317°, and distills without decomposition, under a pressure of 18 mm., at 428°. Under ordinary pressure it boils below 520°. It is insoluble in boiling alcohol, ether, chloroform, and carbon bisulphide, and in cold benzene. It requires more than 100 parts of boiling benzene for solution. The properties of the substance agree with those of benzerythrene, which has been prepared by Schmidt and Schultz by the action of heat on benzene.

From Pinine to Carvacrol. By John L. Mead and Edward Kremers. *Am. Chem. J.*, **17**, 607–611. — The conversion of pinine into pinine nitrosochloride and of the latter into the so-called "nitrosopinine" has been known for some time. Last year Urban and Kremers showed that the "nitrosopinine" was an oxime, and stated that it was converted into a ketone by hydrolysis. The authors prove that the product of hydrolysis is a phenol and not a ketone. A careful study of its physical properties, its sulphonic acid, and dinitro derivative proves that it is carvacrol and not thymol, its isomer. Starting with Wallach's formula for pinine, the transformation to carvacrol through pinine nitrosochloride, pinine isonitrosochloride, and "nitrosopinine" can be easily followed. Constitutional formulæ are given.

Notes on Limonene and its Derivatives. By Edward Kremers. *Am. Chem. J.*, 17, 692–697. — Pure limone was obtained from commercial "carvene" by fractional distillation. The fraction boiling between 174.5°–175° was used in all experiments. Its specific gravity at 20° was .8456. The value of $[\alpha]_D$ was + 120.466 and not + 106.80, as stated by Wallach and Conradi. The rotary power of solutions of varying concentrations in absolute alcohol, chloroform, and glacial acetic acid was determined. It was found that in the case with absolute alcohol and chloroform the rotary power of the limonene diminished with fair regularity as the quantity of solvent increased. With glacial acetic acid no such regularity was observed. The monohydrochloride of limonene when in contact with water in a sealed tube is slowly changed into terpin hydrate. The easy transformation of limonene into carvene the author considers an argument in favor of the formula for limonene, Δ 1, 3 Terpadine, put forward by himself some time ago, and which has been recently suggested by Baeyer.

Scheme for the Identification of Acetanilide, Phenacetine, Quinine Sulphate, Etc. By F. S. Hyde. *J. Am. Chem. Soc.*, 17, 933–935. — The author presents a scheme for the identification of acetanilide, exalgine, phenacetine, phenecoll hydrochloride, salol, resorcin, quinine sulphate, and antipyrine. The melting point, the solubility in water, and the reactions of the solution when boiled with an excess of potassium hydroxide and a few drops of chloroform, when treated with ferric chloride, with dilute nitric acid, and with bromine water, are given for each substance. The application of these tests is sufficient for the identification of the above compounds.

On the Action of Bromine on Metanitraniline. By H. L. Wheeler. *Am. Chem. J.*, 17, 697–704. — When one molecule of metanitraniline dissolved in glacial acetic acid is treated with one molecule of bromine, the chief product is the hydrobromide of monobrommetanitraniline [NH_2, NO_2, Br : 1, 3, 6]. In all previous investigations the nitraniline was brominated in hydrochloric acid solution, and *s*-tribrommetanitraniline was formed. Orthobrommetanitraniline dissolves readily in ether, chloroform, or benzene, less readily in alcohol, and difficultly in ligroïn and in water, from which it crystallizes in hairlike, golden-yellow needles; it is volatile with steam, and has a remarkable sweet licorice taste. The chloride and sulphate of the new base are decomposed by water. The chloride and sulphate of *s*-tribrommetanitraniline, which was formed in small quantity when metanitraniline was brominated as indicated above, were prepared, but not analyzed, on account of their great instability. The acetyl derivative was not completely decomposed when heated with nitric acid to 200°–250° for several days. An attempt to prepare the dibrom substitution-product was unsuccessful. The investigation contradicts the statement which has been frequently made, that meta substituted anilines behave like aniline when exposed to the action of the halogens.

On the Composition of Pelagine. By A. B. Griffith and Charles Platt. *J. Am. Chem. Soc.*, 17, 877. — Pelagine, the violet pigment of Pelagia, was analyzed and found to have the composition $C_{20}H_{17}NO_7$. Pelagine is soluble in carbon disulphide, alcohol, ether, and acetic acid. Its solutions are decolorized by exposure to light, and on spectroscopic examination do not yield characteristic absorption bands. It apparently has no respiratory function, and probably is a lipochrome or a nitrogenous derivative of that class.

Periodides of Pyridine. By A. B. Prescott and P. F. Trowbridge. *J. Am. Chem. Soc.*, **17**, 859–869. — The preparation and properties are described of pyridine methyl pentiodide ($C_6H_5N.CH_3I.I_4$), diiodide ($C_6H_5N.CH_3I.I$), triiodide ($C_6H_5N.CH_3I.I_2$), and octaiodide ($C_6H_5N.CH_3I.I_7$), of pyridine ethyl triiodide ($C_6H_5N.C_2H_5I.I_2$), and of pyridine tetraiodide ($C_6H_5N.I_4$).

The Electrolytic Reduction of Paranitro Compounds in Sulphuric Acid Solution. By Arthur A. Noyes and John T. Dorrance. *J. Am. Chem. Soc.*, **17**, 855–859. — Noyes and Clement showed some time ago that nitrobenzene in sulphuric acid solution is transformed by electrolytic hydrogen into paraamidophenolsulphonic acid. Later Gattermann and his students proved that in general aromatic nitro compounds act in an analogous way, one of the oxygen atoms of the nitro group always migrating during the reduction to the para position with the production of a hydroxyl group. The purpose of the investigation was to determine the nature of the reduction products when the para position was occupied. Three paranitro compounds had already been studied. Paranitrotoluene gives a condensation product of the compound $NH_2.C_6H_4.CH_2OH$ with nitrobenzene. When paranitroorthotoluidine is reduced a hydroxyl group is introduced in the *ortho* position to the amido group. This is exceptional. The carboxyl group in paranitrobenzoic acid is replaced by hydroxyl, the product of reduction being a sulphonic acid of paraamidophenol. In the present paper the authors describe the reduction products of paranitraniline, paranitrophenol, and parachlornitrobenzene. To effect the reduction a current of one or two amperes was passed through a solution of the substance in strong sulphuric acid for forty or fifty hours. Paranitraniline gave the sulphate of paradiamidobenzene. Paranitrophenol and parachlornitrobenzene yielded the same reduction product, the sulphonic acid of paraamidophenol. It is a striking fact that when the group para to the nitro group is negative (Cl or COOH) it is driven out and replaced by hydroxyl.

On the Oxidation of Some Gases with Palladinized Copper Oxide. By E. D. Campbell. *Am. Chem. J.*, **17**, 681–692. — Hydrogen, carbon monoxide, acetylene, ethylene, propylene, and isobutylene were burned by passing the gases over copper oxide containing 1 per cent. of palladium. In order to control the temperature of the tube it was surrounded by a special form of air jacket. In determining the initial combustion-point of any gas a moderate flow of the pure gas was kept passing through the combustion tube, to the farther end of which was attached a small tube containing glass-wool sprinkled with anhydrous cupric sulphate for the detection of water, followed by a U tube containing a clear solution of calcium hydrate for the detection of carbon dioxide. It was found that the presence of the palladium lowered the ignition point of hydrogen from 175°–180° to 80°–85°, that of ethylene from 315°–325° to 240°–250°, of propylene from 270°–280° to 220°–230°, of isobutylene from 320°–330° to 270°–280°, while that of carbon monoxide was not affected. The rate of combustion of each gas was also determined. The fact that acetylene does not burn at once to carbon dioxide and water rendered a comparison of the conduct of this gas with that of the others impossible. Experiments with acetylene, conducted at different temperatures, are described in detail. After the temperature of ignition and rate of combustion of the ordinary gases have been obtained, the author proposes to work on mixtures of these gases in order to determine, if possible, to what extent they may be separated by fractional combustion.

Investigations on the Sulphonphthaleïns. V. On Sulphonphthaleïn and Some Related Compounds. By JOHN WHITE, JR. **VI. Sulphonphthaleïns Derived from Orthosulphoparatoluic Acid.** By WALTER JONES. *Am. Chem. J.*, **17**, 545–569. — This article contains the fifth and sixth contribution from the laboratory of the Johns Hopkins University on the subject of the sulphonphthaleïns. In the first part of the paper (V) the action of bromine on sulphonfluoresceïn and the condensation-products of resorcinol with orthosulphobenzoic acid are described. When sulphonfluoresceïn, prepared by heating dioxybenzoylbenzenesulphonic acid, $(OH)_2C_6H_3CO.C_6H_4SO_3H$, to 160°–170°, was treated with bromine in glacial acetic acid a dibrom, and probably a monobrom, derivative were obtained, whereas fluoresceïn gives a mono, di, and tetra derivative. The action of acetic anhydride on dibromsulphonfluoresceïn gave a product insoluble in alkalies, and therefore probably an acetyl derivative, but the analyses did not give figures agreeing with any probable formula. Phosphorous pentachloride acts on sulphonfluoresceïn readily at 125°–130°, and causes the substitution of chlorine for the two hydroxyl groups and for the anhydride oxygen. It was thought that by mixing dioxybenzoylbenzenesulphonic acid with resorcinol a better yield of sulphonfluoresceïn would be obtained, as the formation of the latter from the dioxy acid involved the splitting off of orthosulphobenzoic acid. It was found, however, that at least two products were formed. This led to a careful study of the action of resorcinol on orthosulphobenzoic acid. Fahlberg and Barge found that when the acid is heated with two or four molecules of resorcinol a condensation-product containing four resorcinol residues is formed, $C_{31}H_{20}O_8S + 4H_2O$. The author repeats the work, and finds that when four molecules of resorcinol are used six residues are introduced, and the resulting compound has the formula $C_{43}H_{28}O_{10}S + 3\frac{1}{2}H_2O$; when two molecules are used four residues are introduced and the compound $C_{31}H_{20}O_8S + H_2O$ is formed. Throughout the work great difficulty in the purification of the compounds was encountered, and the analyses in many cases do not agree closely with theory. In the second part of the paper (VI) experiments with the sulphonphthaleïns derived from orthosulphoparatoluic acid are described. Methylsaccharin, $C_6H_3(CH_3)\langle\begin{matrix}SO_2\\CO\end{matrix}\rangle NH$, was boiled with dilute hydrochloric acid and the resulting acid ammonium salt heated with two molecules of resorcinol; the ammonium salt of paramethyldioxybenzoylbenzenesulphonic acid was formed according to the following equation:

$$C_6H_3(CH_3)\langle\begin{matrix}COOH\\SO_3NH_4\end{matrix} + C_6H_4(OH)_2 = C_6H_3(CH_3)\langle\begin{matrix}CO.C_6H_3(OH)_2\\SO_3.NH_4\end{matrix} + H_2O.$$

A water solution of this ammonium salt was treated with finely powdered minium, and a complicated basic salt containing three atoms of lead was obtained. When an acetic acid solution of this salt was boiled with lead oxide a part was changed into a second basic salt soluble in hot water, $PbO_2.C_6H_3CO.C_6H_3.CH_3.SO_3.Pb.OH$. The lead was precipitated with hydrogen sulphide, and with the free acid so obtained the barium, calcium, silver, zinc, and neutral lead salt were prepared. The sulphonphthaleïn formed by heating the acid was studied with results analogous to those described above. Resorcinol condensed with orthosulphoparatoluic acid in the same way that it did with orthosulphobenzoic acid.

Paranthracene or Dianthracene: A Polymeric Modification of Anthracene. By W. R. ORNDORFF AND F. K. CAMERON. *Am. Chem. J.*, **17**, 658–680. — Paranthracene, made by exposing purified anthracene sus-

pended in benzene and xylene in thin white glass bottles to the action of the sunlight for two or three weeks, after six crystallizations from boiling benzene, was found to have the same percentage composition as anthracene. The pure product was a white crystalline substance, melting at 242°–244° to a light yellow liquid, which, on cooling, solidified to a hard mass, which melted sharply at 213°, being thus transformed into anthracene. Pure paranthracene shows no trace of violet fluorescence, so characteristic of anthracene, nor does it give an addition-product with picric acid. It is sparingly soluble in the hydrocarbons of the benzene series, ethylene bromide, pyridine, anisol, phenetol, and dimethylaniline. It crystallizes in the orthorhombic system, and has the specific gravity of 1.265 at 27°. Unsuccessful attempts to bring about the transformation of anthracene to paranthracene by other methods than the action of sunlight are described. The molecular weight of paranthracene was determined in ethylene bromide, pyridine, anisol, and phenetol, with 357 as an average of thirty determinations ($C_{28}H_{20} = 356$). Paranthracene is therefore *dianthracene.* In order to settle the question whether this peculiar transformation is characteristic of anthracene or is found in the derivatives of this hydrocarbon and in other hydrocarbons, solutions of anthraquinone, dihydroanthracene, dichloranthracene, and anthranol were exposed to the action of sunlight for weeks. In none of these solutions was any change noticed except in the case of anthranol, where a white crystalline substance, which was probably dianthranol, was precipitated. Solutions of pure phenanthrene, retene, camphor, and phenylacridine were also found to suffer no change. When solutions of acridine, $C_{13}H_9N$, which resembles anthracene closely, were exposed to the sunlight a light yellow crystalline precipitate was obtained. It is an open question whether this substance is diacridine or whether it is identical with insoluble hydroacridine obtained by Graebe and Caro. Considering the reactions and properties of anthracene and its easy transformation into paranthracene, the following formulæ of the two substances are proposed: Anthracene consists of two benzene rings, with centric bonds, joined to each other in the ortho position by two CH groups, the carbon atoms of which are united. In the transformation to paranthracene this para bond in the middle ring is broken, and the free affinities of two molecules unite to form the double molecule.

The Action of Magnesium upon the Vapors of the Alcohols and a New Method of Preparing Allylene. By Edward H. Keiser and Mary B. Breed. *J. Franklin Inst.*, 139, 304–309. — The vapor of methyl alcohol was passed over magnesium. When the temperature was raised to dull redness the magnesium began to glow, and finally became red-hot throughout its entire mass. After cooling, the residue was a black, coherent mass, which evolved a rapid current of gas when brought into water containing a drop of ammonium chloride. This gas had the odor of acetylene, but when conducted through an ammoniacal solution of cuprous chloride greenish-yellow cuprous allylide was formed; an ammoniacal solution of silver nitrate gave the corresponding silver salt as a white crystalline precipitate. Both compounds dissolved readily in dilute acids with evolution of allylene, C_3H_4. While the magnesium was glowing in the alcohol vapors a large amount of gas was given off, which proved to be almost entirely hydrogen and methane. When iron or zinc was used instead of magnesium the gases consisted of a mixture of hydrogen and carbon monoxide, with a trace of methane and carbon dioxide. The action of magnesium on ethyl, propyl, amyl, allyl, and isobutyl alcohols was also studied. In all cases the metal was changed

into a compound which gave off allylene when treated with water. Allyl alcohol gives the largest yield of the silver compound, which is used in the preparation of the pure gas, and the authors therefore propose this method as the best for making allylene. The gases formed during the action of the magnesium on the vapors varied with the different alcohols, and also were different from the products formed when iron or zinc was used. The most striking difference is the small amount of carbon monoxide formed in the first case.

Crystalline Compounds of Sucrose, Dextrose, and Levulose. By F. G. Wiechmann. *School Mines Quart.*, **16**, 233–234. — Some time ago the author gave an account of a crystalline magma which was formed in an inverted sucrose solution under the influence of sunlight (*School Mines Quart.*, 13, No. 2). He has since separated the crystals from the adhering liquid, and finds that they consist of sucrose, 5 to 16 per cent.; dextrose, 59 to 60 per cent.; levulose, 21 to 34 per cent. The liquid in one experiment contained 32 per cent. sucrose, 22 per cent. dextrose, and 41 per cent. levulose.

Glutarimide. By R. Seldner. *Am. Chem. J.*, **17**, 532–535. — Glutarimide was prepared by the methods used by Miller in the preparation of succinimide (*J. Am. Chem. Soc.*, **16**, 443). Mixtures of glutaric acid and aceto nitrile, glutaric nitrile and acetic acid, and glutaric acid and glutaric nitrile were heated in sealed tubes, in the presence of a few drops of acetic anhydride, to 200°–210° — for four hours in the case of the first two mixtures, and for nine hours in the case of the last. The second method of preparation gives the best results.

On the Oxidation of Complex Carbohydrates. By G. de Chalmot. *Am. Chem. J.*, **17**, 535–539. — The author has recently advanced the hypothesis that pentose molecules are formed in plants, by oxidation, from complex molecules of hexosans in which a part or all of the aldehyde groups have been bound by condensation, and therefore protected from further oxidation. The pentoses are probably formed from the hexoses by the alcohol group at the end of the hexose molecule being oxidized to aldehyde and carboxyl, and by the splitting off of carbon dioxide. Experiments were undertaken to test this hypothesis, but as they were interrupted in an early stage the results are published and the field left to others. Starch, saccharose, and *a*-methyl-d-glucoside were cautiously oxidized with an alkaline solution of bromine. In each case there was an evolution of carbon dioxide, and a solution was obtained which reduced Fehling's solution in the cold and gave an osazone when treated with phenylhydrazine.

The Occurrence of Trimethylene Glycol as a By-Product in the Glycerine Manufacture. By Arthur A. Noyes and Willard H. Watkins. *J. Am. Chem. Soc.*, **17**, 890–891. *Tech. Quart.*, **8**, 261–262. *Am. J. Pharm.*, **67**, 633–634. — The authors found 38 per cent. of trimethylene glycol in the "light stuff" obtained in the recovery of glycerine from the lyes of a soap-making firm near Boston, and attribute its occurrence to the fermentation of the glycerine in the fat before saponification.

Action of Sodic Alcoholates on Chloranil. Acetals Derived from Substituted Quinones. By C. Loring Jackson and H. S. Grindley. *Am. Chem. J.*, **17**, 579–607, 633–658. — Dichlordiphenoxyquinone, $C_6Cl_2(OC_6H_5)_2O_2$, melting at 243°, was obtained by the action of sodium phenylate on chloranil; it gave a hydroquinone when reduced, and when treated

with aniline, sodium malonic ester, or sodium ethylate, the groups OC_6H_5 were replaced without the elimination of the chlorine. From the salt formed by the action of sodium methylate the free acid was precipitated. The authors consider this to be a *hemiacetal*, and assign to it the following formula: $C_6(OCH_3)_4$ [1, 3, 4, 6] $(OH)_2$ [1, 4] Cl_2 [2, 5]. All the chemical reactions of the substance are in accord with this view, and cannot be explained by assuming the presence of two carbonyl groups. When heated it loses two molecules of alcohol, and is changed into dichlordimethoxyquinone. The benzoyl ether is stable, and does not yield an oxime or a hydroquinone. The study of these hemiacetals has led the authors to propose analogous constitutional formulæ for quinhydrone and phenoquinone. In favor of this view is the fact that one molecule of quinone unites with one molecule of a diatomic phenol, hydroquinone, with two of a monatomic phenol, methylhydroquinone, and does not combine at all with such compounds as dimethylhydroquinone. The instability of the compounds and their salts is further evidence. By the action of ethyl iodide on the silver salt of the hemiacetal a tetraethylacetal, $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$, was obtained, which was stable in the presence of alkalies, but was decomposed by acids with the formation of dichlordiethoxyquinone. Dichlordiethoxyquinone dibenzoyldiethylacetal, $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2$, was formed from the sodium salt and benzoyl chloride; dilute sulphuric acid decomposed it to the compound $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2O$, which on reduction gave a substance with the probable formula $C_6Cl_2(OC_2H_5)_2OH(OCOC_6H_5)_2$. If chloranil is treated with four molecules of sodium phenylate, tetraphenoxyquinone is formed. This can be reduced to the corresponding hydroquinone, and when boiled with sodium hydroxide is converted into diphenoxanilic acid, $C_6(OC_6H_5)_2(OH)_2O_2$. *Experimental Part*: Dichlordiphenoxyquinone, $C_6Cl_2(OC_6H_5)_2O_2$, was obtained as a red precipitate when one molecule of chloranil suspended in water was treated with two molecules of potassium phenylate. It crystallizes from benzene in needles melting at 243°, is saponified by sodium hydroxide forming chloranilic acid, and is reduced by strong hydriodic acid to dichlordiphenoxyhydroquinone, $C_6Cl_2(OC_6H_5)_2(OH)_2$, which crystallizes in colorless prisms melting at 197°–198°. Dichlordiphenoxyquinone was treated with aniline with the expectation of removing the two remaining atoms of chlorine. Dichlordianilidoquinone, $C_6Cl_2(C_6H_5NH)_2O_2$, which had been previously prepared by Hesse, Knapp, and Schultz, was formed. Sodium malonic ester gave a blue precipitate of the sodium salt of dichlorquinonedimalonic ester, from which the ester, yellow needles soluble in alcohol, melting at 130°, was obtained. Hydriodic acid transformed it into a hydroquinone, and sodium carbonate into diethoxyquinonedimalonic ester, $C_6(OC_2H_5)_2[CH(COOC_2H_5)_2]_2O_2$, yellowish white needles melting at 115°. Dichlortetramethoxyhydroquinone, $C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$, formed by the action of sodium methylate on dichlordiphenoxyquinone, is a white amorphous substance, which is transformed into the red dichlordimethoxyquinone when heated to 160°, or when warmed with water, alcohol, or acetic acid. The sodium and silver salts were made. The diethylacetal, and acetals containing ethyl and methyl groups, and a number of their salts and derivatives analogous to those of the dimethylacetal described above, were prepared.

Tetrinic Acid. By Paul C. Freer. *Am. Chem. J.*, **17**, 779–796. — In order to furnish further evidence in favor of his formula for tetrinic acid, $CH_2.C(OH):C(CH_3).CO.O$, the author has subjected the action of bromine

on methylacetoacetic ester to a careful revision, and has come to conclusions which differ from those of Nef. According to the latter, no hydrobromic acid is formed when the sodium salt of methylacetoacetic ester is brominated, and the resulting compound is therefore an *a*-substitution-product. When the sodium salt was treated with one half the calculated quantity of bromine, an oil, consisting mainly of free methylacetoacetic ester and a small amount of the brominated product, and a considerable quantity of tetrinic acid were obtained; when one molecule of bromine was used the product distilled much as Nef described, with the exception that it had no constant boiling point. The formation of free methylacetoacetic ester shows that hydrobromic acid must have been present during the first part of the reaction, and consequently γ-brommethylacetoacetic ester must, at least in part, have been formed. In brominating free methylacetoacetic ester it was found that the fraction of a Kahlbaum preparation boiling at 84°–85° (25 mm.) gave results quite different from those obtained when the fraction boiling at 85°–87° (25 mm.) was used. In the first case an oil boiling at 107°–112° (30 mm.), which gave analytical results agreeing with monobrommethylacetoacetic ester, and a small quantity of tetrinic acid were obtained; in the second case, when the temperature of the oil bath had reached 120° (30 mm.) the pressure fell to 70 mm., a violent ebullition of ethyl bromide took place, and the contents of the flask, which proved to be tetrinic acid, became solid. A sample of methylacetoacetic ester prepared by the author did not yield any tetrinic acid when brominated, but a product without a constant boiling point (107°–109° at 30 mm.). The difference between the different samples of apparently equally pure ester the author explains by assuming the presence of two geometrical isomers. When brommethylacetoacetic ester was treated with sodium the resulting product consisted of methylacetoacetic ester, its monobrom derivative, and a thick oil without a constant boiling point, which was not investigated. The formation of hydrogen during the reaction and the fact that oxalic acid was one of the products of oxidation of brommethylacetoacetic ester showed that some of the γ-substitution-product must have been present. As a final proof that the substance obtained by direct bromination of methylacetoacetic ester is a mixture of the *a*- and γ-brom derivative, an ethereal solution of the pure substance of Nef, boiling at 107°–108° (30 mm.), was extracted with 10 per cent. caustic soda solution and immediately neutralized with sulphuric acid. An oil separated from the alkaline solution which, on distillation, had a higher boiling point than the brom ester and left a considerable residue of tetrinic acid. The oil, insoluble in alkali, had its boiling point reduced two degrees, and when heated in a sealed tube at 100° was not changed into tetrinic acid unless hydrobromic acid was present. The former the author considers the γ- and the latter the *a*-brom substitution-product. Molecular weight determinations of ethyl tetrinate, benzoyl tetrinate, and tetrinic chloride show that the acid has the simple molecular formula. The two ethyl ethers and two chlorides obtained are explained by stereo-chemical considerations.

Technical Chemistry.

F. H. Thorp, Abstracter.

Arsenic in Glycerol. By G. E. Barton. *J. Am. Chem. Soc.*, **17**, 883–890. — The author reviews briefly the work of Jahns, Ritsert, Vulpius, Siebold, Jaffe, Luttké, and Sanger on arsenic determinations in glycerol and wall paper. He finally adopted a modification of Sanger's method (*Proc. Am.*

Acad., 26, 24) for making arsenic tests, which is essentially a comparison of mirrors obtained in a modification of Marsh's apparatus with those obtained from standard solution of sodium arsenite. It was found that the zinc varied much in its content of carbon, and this caused irregularities in the speed of gas evolution, which resulted in differences in the mirrors. The preparation of standard mirrors at various speeds and under all possible variations is proposed as a remedy for this difficulty. The use of uniform tubes of the hardest obtainable glass is necessary. Formation of two mirrors is avoided by surrounding the reduction tube with an iron or nickel jacket. — Eight samples of glycerol were tested, five showing arsenic present. In one case the method failed to show arsenic in a sample to which arsenic had been added. From this the author concludes that some samples contain, either originally or after the treatment with sulphuric and nitric acids, something capable of holding back the arsenic. He then tried diluting the glycerol with water and adding it directly to the reduction flask, and thus obtained a quantitative result. The colorimeter test with paper saturated with silver nitrate solution was found about five times as sensitive as the Marsh test, but, owing to the rapid action of light, the yellow stain cannot be well compared with permanent standards. Glycerol made from soap lyes is very apt to contain arsenic from the hydrochloric acid used in neutralizing the spent lye.

The Determination of Tannin by Metallic Oxides. By William H. Krug. *J. Am. Chem. Soc.*, 17, 811–814. — The author tried substituting yellow mercuric oxide for hide-powder in the usual shaker method of analysis. After several trials he decided that it was best to shake the mixture four hours, and then to allow it to stand over night before filtering. He used four grams of mercuric oxide and 75 cc. of diluted tannin solution. After filtering, 25 cc. of the filtrate were evaporated to dryness on the steam bath, the residue dried at 100° C. and weighed. The difference between this weight and that of the residue from 25 cc. of the solution before treatment with mercuric oxide was calculated as tannins. Ash determinations were made to detect any of the oxide passing into the filtrate. The results were fairly close even when variations in the conditions were tried. No oxide was found in the filtrate. The end of the reaction is easily seen, as the mass becomes gelatinous and of a dirty brown color. The time consumed is rather more than by the hide-powder process, but the results are claimed to be more uniform. Besides mercuric oxide, the oxides of zinc, lead, and magnesium were tried, but with less satisfactory results. Zinc and lead were very slow in combining with the tannin, while magnesium dissolved and passed into the filtrate, introducing a large error.

An Electrolytic Process for the Manufacture of White Lead. By R. P. Williams. *J. Am. Chem. Soc.*, 17, 835–842. — This is a description of the patented process of A. B. Brown for the electrolytic production of white lead. The process is certainly novel, and should attract the notice of technical chemists. It consists in decomposing by an electric current a solution of sodium nitrate, containing about one pound to the gallon, in wood cells provided with porous diaphragms; the nitric acid radical attacks the positive electrode, which is of metallic lead, and the lead nitrate solution thus formed is later precipitated by the sodium hydrate produced at the other electrode. The precipitated lead hydroxide is digested with bicarbonate of soda solution, whereby lead carbonate in a very fine state of division is obtained. The so-

dium nitrate is thereby regenerated. The sodium bicarbonate used is formed by passing carbonic dioxide into the caustic soda solution. It is claimed that the process can be made a commercial success, the white lead being equal or superior to the old "Dutch process" product. The plant required is small for a considerable output, and there is no loss of time, the reactions taking place rapidly. There is great saving in the matters of labor and materials as compared with the Dutch process. The product of the electrolytic process is in a very fine state of division, and is claimed to be of a spongy character, non-crystalline, and having a greater covering power than Dutch process lead. Tests of durability show this lead to be fully equal to Dutch lead. A short description of Thenard's process follows, and the article is concluded with a discussion of the future of this electrolytic process.

Inspection of Cotton for Use in Manufacture of Guncotton. By Charles E. Munroe. *J. Am. Chem. Soc.*, **17**, 783–789. — The author considers the following examinations essential in inspecting cotton: Optical examination for color, cleanliness, presence of cops, knots, tangles and foreign bodies, length and strength of fiber; odor; moisture; ether extract; soda-lye extract; ash; rate of absorption of water. Ether extract is determined by extraction of a weighed quantity of cotton, with petroleum-ether in a Soxhlet apparatus. Soda-lye extract is obtained by boiling for eight hours with caustic soda solution containing 17.305 grams per liter. Ash is determined by burning the sample with paraffine in a platinum crucible and igniting the residue. Rate of absorption of water is determined by throwing the cotton on the surface of distilled water and noting the time it takes to sink to the bottom. For a smokeless powder it should sink in two minutes. This test shows the relative rate at which the cottons absorb the mixed acids during dipping. Tables of analyses of several grades of commercial cotton show great variations in these several items. Some experiments made with absorbent cotton, to determine its absorptive capacity, showed that one sample retained 15.5 times its own weight of water.

Deterioration of India Rubber and its Causes. By Frank W. Birchall. *India Rubber World*, **13**, 39–40. — The author inclines to the theory that the oxidation of caoutchin is one of the causes of cracking of rubber goods. This caoutchin is soluble in chloroform, but precipitates on adding alcohol. Vulcanization does not diminish its affinity for oxygen. The compounds used in rubber tend to fill its pores and lessen the opportunities for oxidation somewhat, but substances introduced in the compound are often injurious. Examples are given of injury to the rubber due to antimony sulphide which contained sulphuric acid, and in another case to a vulcanizing compound which contained moisture. Excess of sulphur over the amount necessary to vulcanize is liable to cause "bloom" on the finished goods. This may be removed by boiling in caustic soda, but this operation may injure the goods. Oxidizable oils are objectionable in rubber compounds, as the oxidation may go too far. Metallic oxides added for coloring purposes, or left in the cloth after dyeing, may cause injury to the rubber. A table of analyses of sound and damaged rubber shows very large increase in the percentage of oxygen and some loss of carbon and sulphur. The author expresses the hope that rubber may be synthetically produced in the near future.

Examination of Fats Used in the Leather Industry. By W. Schmitz-Dumont. *Leather Manufacturer*, **5**, 179. — This is a brief compilation of the methods of analysis of fats, apparently containing nothing original.

The Reduction of Alumina Considered from a Thermochemical Standpoint. By JOSEPH W. RICHARDS. *J. Franklin Inst.*, 139, 295–304. — The article consists of calculations of the heat effect corresponding to various methods of reduction, and of the minimum temperature at which the reactions become exothermic.

Analyses of Commercial Fertilizers. *Bulletins of the State Agricultural Experiment Stations: Conn., No.* 120; *Ky., No.* 56, *No.* 60; *Maine, Nos.* 18 *and* 19; *Md., No.* 34; *Mass. Hatch Sta., Nos.* 30, 31, *and* 34; *Mass. State Sta., No.* 57; *N. H., No.* 26; *N. Y., Cornell Univ. Sta., No.* 92; *N. C., Nos.* 29 *and* 30; *R. I., No.* 32; *S. C., No.* 20; *Vt., Nos.* 45, 46, *and* 47; *Ore., No.* 36; *W. Va., Special Bull., July 1, 1895; Ind., Special Bull., May, 1895, Perdue Univ.; Ga. Dept. Agr., No.* 30; *Ann. Rep. N. J., No.* 15,; *Ann. Rep. N. Y., Geneva Station, No.* 13. — The foregoing bulletins contain tabulated results of the analyses of fertilizers made during 1895, the name of the brand and of the abstracter being usually stated.

A. H. GILL, ABSTRACTER.

Test of the Amount of Combustible in Smoke. By B. P. FLORY. *Sibley J. Eng.*, 9, 338–340. — The experiments were made by heating the coal in a crucible and collecting the smoke. It is calculated that under the worst circumstances possible about 14.7 pounds of soot, giving 13.700 B. T. U. per pound, would be obtained from one ton of coal, showing the futility of the smoke-consuming devices. The following were the results of the analyses of a sample of St. Louis coal and of the soot obtained from it:

	Moisture.	Ash.	Hydrocarbons.	Carbon.
Coal	4.0	9.0	36.0	51.0
Soot	2.5	61.0	10.5	26.0

On the Physical and Chemical Characteristics of Some California Oils. By WALTER C. BLASDALE. *J. Am. Chem. Soc.*, 17, 935–941. — The author has determined the specific gravity, index of refraction, Maumené figure, viscosity, melting point of fatty acids, iodine absorption, and saponification number of eleven samples of olive oil known to be genuine, of ten samples classed as "commercial," and of several miscellaneous oils — those of the English walnut, acorn, California nutmeg, pine-nut, and yellow and black mustard seed. In addition to the foregoing tests, the elaidin and Bechi were also applied. The iodine figures were in many cases higher than those usually accepted as European standards; the elaidin test gave a cake in some cases only after six hours' standing. The viscosity of the soap solution derived from a definite weight of the oil is found to be very characteristic; for example, the following values were obtained: Cotton seed 280, almond 645, rape seed 670, sesame 415, olive 645–650, expressed in grams of sugar per liter and measured as a torsion viscosimeter. The viscosity method suggested by Professor Rising and worked out by Mr. Babcock is as follows: 15 grams of oil are saponified with 30 cc. water, containing 7.5 grams KOH and 10 cc. alcohol, the resulting mixture washed into an evaporating dish, the alcohol expelled, diluted to 500 cc. at 15°, and the viscosity of the solution determined by a torsion viscosimeter.

The Determination of the Heating Effects of Coals. By W. A. Noyes, J. R. McTaggart, and H. W. Craver. *J. Am. Chem. Soc.*, **17**, 843–849. — The authors state first the various methods which have been employed for this determination, and give their limits of accuracy. They then give the results of their own investigation of six bituminous Indiana coals, comparing the data obtained from Hempel's calorimeter, chemical analysis, and Berthier's test. Many of the figures given are the results of three fairly concordant determinations, and in all cases of at least two. The differences between the results of chemical analysis and the calorimeter varied from +2.6 to −4.6 per cent., and in three other cases by ±1.2 per cent. Between Berthier's test — the reduction of litharge — the variations were from +2.1 to −2.3 per cent., an average of about ±1 per cent. being obtained in the other cases. The authors call attention to the fact that it is impossible to burn anthracite coal in the Hempel calorimeter, owing to the fact that it cannot be compressed into the form of cylinders. With the Thomson-Barrus calorimeter a deposit of carbon is produced; they think, however, that it would give satisfactory results with anthracite coals. The abstracter has experienced the same trouble with both calorimeters, but has found that it can be remedied in the Thomson-Barrus by very careful manipulation. With anthracite coals, however, in the latter apparatus an ash is formed over the surface of the coal which effectually prevents its further combustion.

Naphthalene: The Causes of its Formation and Means of its Prevention in a Free State in Illuminating Gas. By C. P. Russell. *Am. Gas Light J.*, **63**, 970. — The chief disadvantage of this "annoying impurity" lies in its clogging up the purifying apparatus in the works and the service pipes; in addition, it lowers the candle power of the gas. The coal, particularly if slack, should not be wet, and the charges not too great. The substance appears thus to be formed by the imperfect distillation of coal; for, when the products are thoroughly heated, the quantity formed is small. The remedy is either then through distillation or more complete cooling and scrubbing of the gas. The presence of naphthalene in the gas liquor can be shown by treating it with nitric acid and subsequently supersaturating with hydrochloric acid. Upon dipping into the solution a splinter of fir wood it is tinged a rich purple.

G. W. Rolfe, Abstracter.

Acidity of Glucose Syrup and Grape Sugar. By H. E. Horton. *J. Am. Chem. Soc.*, **17**, 402–403. — The author gives the figures of about fifty acidity determinations of commercial glucose sirups and sugars from three different manufacturers, and discusses the nature and origin of the free acid.

Ash in Glucose Syrup and Grape Sugar. By H. E. Horton. *J. Am. Chem. Soc.*, **17**, 403–405. — Ash determinations of samples from four manufacturers are given. The explanation of the nature of this ash, while applicable to but a few of the samples discussed, is most interesting.

On the Estimation of Extraction in Sugar Houses. By M. Trubek. *J. Am. Chem. Soc.*, **17**, 920–923. — The author describes the method of Icery by which extraction is calculated by determining the per cent. of fiber in the cane and the weight of fiber in a sample of the wet bagasse, and points out that when the bagasse from the first mill is macerated Icery's formulæ are in-

applicable. The author, however, shows how the extraction can be calculated in such cases by a series of ingenious but difficult and complicated algebraic equations, requiring as data, besides the two fiber determinations, estimations of sucrose in the cane, juice, and macerated bagasse. This calculation is based on the assumption that the quotient of purity of the juice is unchanged by maceration. Making as probable an assumption that the dilution of the juice extracted is the same as that of the juice in the bagasse, the reviewer suggests a much simpler method based on an application of Icery's formulæ — determining the weight of diluted juice in the bagasse — the per cent. of water in this juice by calculation of the Brix of the undiluted juice from the first mill ($B_{/}$), and of the diluted juice ($B_{//}$) by the formula $P = \frac{B_{/} - B_{//}}{B_{//}}$, and hence the weight of undiluted bagasse. However, as the author hints, these indirect methods of determining juice extraction, while attractive, are at best approximate, owing to the great difficulty of obtaining a fair sample for fiber determinations, especially of the cane.

Biological Chemistry.

E. H. Richards, Abstracter.

Alfalfa. *U. S. Dept. Agric., Div. Agrostology; Farmers' Bull. No.* **31**, 1–23. — Alfalfa is a nitrogen collector, and seems to have great power of adaptation to different soils, as shown in the variation in the amount of mineral matter it takes from different soils. The ash of that grown on granitic soil showed potassium carbonate 48.42 per cent., and calcium carbonate 13.42 per cent., while that grown on clayey soil, with chalk, gave an ash containing potassium carbonate 20.60 per cent., calcium carbonate 49.68 per cent. Alfalfa hay cut when the plant was beginning to bud yielded: Water, 8.11 per cent; ash, 11.62 per cent.; fat, 3.61 per cent.; albuminoid nitrogen, 18.19 per cent.; crude fiber, 12.88 per cent.; nitrogen, free extract, 45.59 per cent.

The Distribution of the Salts in Alkali Soils. *Cal. Agric. Exp. Sta., Bull. No.* **108**, 14. — The great obstacle to the cultivation of large tracts of land in the Rocky Mountain region is the presence of alkali salts. A careful study of the means of keeping these salts at such a depth as not to interfere with the growth of the crops has been made at Tulare, with the result that the control of loss of moisture from the surface by evaporation is the simplest means yet found.

Soil Moisture. *U. S. Dept. Agric., Bull. No.* **3**, 1–23. — The average per cent. of moisture in soil in Virginia suited to the growth of garden truck was for June, 1895, 8.7, and for July 8.6, while soil in Kentucky, taken as a type of grass land, contained for the same periods 19.7 and 20.4 per cent. Charts are also given for twenty stations in seven different States showing the amount for each day in the month of July.

S. C. Prescott, Abstracter.

Some Derivatives of Chimaphilin. By W. E. Ridenour. *Am. J. Pharm.*, **67**, 236–242. — The chimaphilin used in this investigation was procured by distilling coarsely-ground Chimaphila umbellata (Prince's Pine) with water and collecting the crystals. A chlorine derivative was obtained by

passing pure, dry chlorine gas through a solution of the crystals in absolute ether. The solution was partially decolorized, and on evaporation yellow needle-shaped crystals, melting at 93° and 94° C., remained. They were soluble to some extent in a 10 per cent. solution of caustic potash. When the solution in KOH was acidified with HNO_3 and treated with $AgNO_3$ a distinct precipitate of AgCl was formed. It appears that the compound formed is a tetra-chlor addition-product, $C_{24}H_{21}O_4Cl_4$. With acetic anhydride there is no change of composition. Nitric acid produces yellow crystals, with melting point of 154° C., probably a nitro-derivative of an oxidation-product of chimaphilin.

The Tannin of Cloves. By W. L. Peabody. *Am. J. Pharm.*, **67**, 300–306. — The results of the experiments of the author may be expressed in the following statements: (1) The amount of tannin present in cloves varies from 10 to 13 per cent. of the weight of the spice as found in the market. (2) The tannin of cloves has the same percentage composition as gallotannic acid, and yields the same products by treatment with various reagents as does that compound; hence they are probably identical.

Anatolian Licorice Root. By J. W. Nickum. *Am. J. Pharm.*, **67**, 306–311. — This is a short article dealing chiefly with the pharmaceutical nature of the plant. A proximate analysis only is given, and a comparison is drawn between this and some other varieties of licorice root.

Chinquapin. By Henry Kraemer. *Am. J. Pharm.*, **67**, 453–459. — The author finds that the nut of chinquapin (*Castanea pumila, Mill.*) contains 18.17 per cent. moisture, 6.95 per cent. fixed oil, 36.37 per cent. starch (resembling wheat starch), and 2.35 per cent. nitrogen.

Examination of Elm Bark, Flaxseed, and Mustard for Starch. By J. M. Lloyd. *Am. J. Pharm.*, **67**, 459–464. — Dried elm bark was found by the author to give a color reaction for starch when treated with iodine, especially if a little sulphuric acid was present. In the absence of the acid the color is not permanent, since other compounds, probably tannin and an organic calcium compound, interfere with the reaction. Elm bark yields 8.86 per cent. ash. Pure flaxseed was found to contain no starch, but the commercial ground-product responded to the test in every case examined. Mustard when pure was also found to be free from starch. Oil of mustard, even in presence of starch, takes up iodine, thus giving a negative starch test.

Taxaracum Root and Taxaracin. By L. E. Sayre. *Am. J. Pharm.*, **67**, 465–468. — It is found that the root of taxaracum contains a coloring matter very sensitive to acids and alkalies, and varying in amount with the season, that obtained in late autumn being far greater in quantity than that of early fall. An acrid principle, and a bitter principle, taxaracin, were also isolated. The latter gave glucosidal reactions, but could not be separated out by the usual process.

The Tannin of Cinnamomum Cassia. By T. R. Thornton. *Am. J. Pharm.*, **67**, 400–403. — The author has studied the tannin separated from cinnamon, and made comparisons between it and gallotannic acid and white oak tannin. He finds that it corresponds the more nearly to the oak tannin in its general behavior toward reagents.

Chemical Analysis of Some Commercial Varieties of Cacao. By W. E. Ridenour. *Am. J. Pharm.*, 67, 207–209. — The author has subjected several varieties of cacao to chemical examination, with the following average results: Fat, 42.99 per cent.; theobromine, 0.97 per cent.; albuminoids, 10.51 per cent.; glucose, 1.40 per cent.; saccharose, 1.29 per cent.; starch, 4.27 per cent.; lignin, 5.95 per cent.; cellulose, 14.44 per cent.; extractive matter, 9.30 per cent.; moisture, 5.18 per cent.; ash, 3.70 per cent.

Metallurgical Chemistry and Assaying.

H. O. Hofmann, Abstracter.

Temperature of Lead Slags. By M. W. Iles. *School Mines Quart.*, 17, 20–25. — This is an attempt to measure by calorimetric methods the temperature of a lead slag as it flows from the blast furnace. The results obtained differed considerably, the general average temperature being 1,034° C.

Temperature of Gases from Lead Furnaces. By M. W. Iles. *School Mines Quart.*, 17, 19–20. — The temperature of gases from two blast furnaces of the Globe Smelting and Refining Company, Denver, Colorado, was measured for about a month and found to average 101° C. It increased about 40° C. when the sides of the furnaces became coated with wall accretions, as was natural.

The Brown-DeCamp Fume Collector. By the Editor. *Eng. Mining J.*, 60, 373. — The minimum loss of metal in smelting lead ores in the blast furnace in this country is 6 per cent. In order to obtain a higher extraction, filtering of furnace gases has been resorted to in several instances. The collector described and illustrated in the article was introduced about a year ago at the Omaha (Nebraska) works of the Grant and Omaha Smelting and Refining Company, and has given satisfactory results. The leading facts are given in the paper.

A Possible Explanation of Kernel-Roasting. By M. A. Knapp, G. McM. Ross, H. M. Howe, and W. Edwards. *Eng. Mining J.*, 59, 339, 340, 364, 411. — Referring to the theory of Mr. Howe (*Tech. Quart.*, 8, 111), that capillarity and surface tension are the cause of the forming of a kernel rich in copper in roasting pyritic ores, Mr. Knapp calls attention to the observations made in examining microscopically porphyritic rocks, where a semi-fused mass has shown the tendency to absorb solid particles, differing from it in chemical composition, and distribute them again throughout the whole without any flowing taking place. Assuming this tendency to be also inherent in copper-bearing pyrite surrounded by a semi-fused mass of sulphide, he argues that the solid center is attacked by the viscid shell and the absorbed material equally redistributed. Iron on the outside of the shell being continually oxidized becomes inert, while the copper is redistributed toward the center. The result of this chemical interchange is a concentration of copper in the center of a dump without the flow of cuprous sulphide, which Plattner assumed and for which Howe gave a theory. — Mr. Ross does not accept Mr. Howe's criticism, that there is no ground for saying that magnetism is the cause of the concentration of the copper in the kernel. His experiments in magnetic concentration of roasted copper-bearing pyrites gave results precisely opposite to those of Mr. Howe. In the most favorable tests the mag-

netic part, 19 per cent. of the original ore, assayed over 36 per cent. copper, while the average gave equal weights of magnetic and non-magnetic ore with equal assays. Further, at his works in Copperopolis, California, he found that in the heaps the best formed and richest kernels had shells that showed the least magnetic attraction. Again, high-grade kernels heated to below their temperature of ignition often became true magnets, *i. e.*, were able to attract and hold each other and particles of iron, retaining this property at ordinary temperatures; they lost their magnetizing force when heated to where the sulphur began to be driven off, but were still magnetizable, *i. e.*, attracted by the magnet. — Mr. Howe, in correcting his own criticism, based on an accidentally mistaken deduction from results obtained by himself, thinks Mr. Ross' theory reasonable, if cuprous sulphide is magnetic, not only magnetizable, when in the plastic state. Perhaps magnetic attraction and surface tension may act together. — Mr. Edwards' theory is that the oxidized copper is drawn toward the interior by its affinity for sulphur, which is present there in abundance. He calls attention to the fact that the rind is richer in silver than the kernel, and that the silver is present often in the metallic state in the form of globules.

Magnetic Oxide of Iron in Copper Mattes. By E. Keller. *Eng. Mining J.*, **60**, 465. — The author calls attention to two leading characteristics of Montana copper mattes, viz., that the percentage of sulphur remains a pretty constant figure (from 22.12 to 23.88 per cent., with copper varying from 29.41 to 60.22 per cent.), and that considerable magnetic oxide of iron is found in low-grade matte. This he considers justifies him in putting Fe_2O_3 into the general formula. — A considerable number of matte analyses accompany the paper, and the method of determining magnetic oxide of iron is given in detail.

An Improved Ten-Ton Chlorination Barrel. By J. E. Rothwell. *Eng. Mining J.*, **60**, 370. — The barrel described and illustrated in the paper has a capacity of ten tons. Hitherto the largest vessels used in barrel-chlorination have held five tons. By doubling the capacity the treatment of ore is considerably cheapened, which is an important matter with the large masses of low-grade refractory gold ores.

Fractional Precipitation of Gold from a Solution Carrying Gold and Copper with Hydrogen Sulphide. By J. E. Rothwell. *Eng. Mining J.*, **60**, 323. — The difficulty hitherto experienced in the use of hydrogen sulphide as a precipitant, that copper falls out with gold and forms a bulky precipitate requiring a lengthy process for treatment, has been overcome by Mr. Rothwell, with the aid of fractional precipitation. In the laboratory with two or three liters solution it is hardly possible to precipitate gold alone with hydrogen sulphide; in the works, however, with tanks holding from five to seven thousand gallons, all the gold is readily precipitated, with only a very small amount of copper. In chlorinating in barrels an ore of the following composition: SiO_2, 88.35; Al_2O_3, 2.65; Fe_2O_3, 6.05; CaO, 0.55; MgO, 0.25; Cu, 0.35; As, trace; Sb, 0.05; S, 0.90, after crushing through a 24-mesh sieve and washing in a Pearce turret furnace, the filtered solution of twenty-four tons of ore about filled a precipitating vat holding seven thousand gallons. The solution was strongly acid and had a rich, yellowish blue color, and contained about 75 per cent. of the copper of the ore, or about 126 pounds copper and about 72 ounces gold. After removing the free chlorine and reducing the higher chlorides with sulphurous acid, the gold was precipitated with hydrogen sulphide generated from 4 pounds iron sulphide, 15

pounds concentrated sulphuric acid, and from 60 to 70 pounds of water. About 70 per cent. of the roasted sulphide precipitate was obtained in the form of bullion, which was from 830 to 960 fine, showing that comparatively little copper had been precipitated. In testing to see if all the gold had fallen out, a sample from the precipitating vat was filtered and the filtrate divided between two 3-ounce beakers, placed on a sheet of white paper, and ferrous sulphate added to one, when no trace of gold could be discovered. Fractional precipitation has further the advantage in that the filtrate from the sulphide can be used again with a new charge, a thing to be considered in regions where water is scarce. The paper contains many practical details supplementing previous papers by the author, who for many years has been a specialist in this branch of metallurgy.

Contributions to the Chemistry of the Cyanide Process. By E. A. SCHNEIDER. *Eng. Mining J.*, **60**, 489, 514. J. C. WELLS. *Ibid.*, 559. — The paper is a record of some experiments carried out to see whether the oxygen necessary for the solution of gold in potassium cyanide oxidized this to cyanate, and to find what effect the carbonic acid of the air has on cyanide solutions. The results show that oxygen does convert cyanide into cyanate, but not to such an extent as is generally believed, and that the action is stronger with dilute than with concentrated solutions. The effect of the carbonic acid of the air on cyanide is very marked. With an undisturbed surface weak solutions are acted upon more slowly than concentrated ones; with an agitated solution the reverse is the case. Experiments proved that a film of oil protected cyanide very effectively from the action of the air. A last set of tests showed that carbonic acid acting on cyanide gives potassium bicarbonate and hydrocyanic acid, and that the two products can exist side by side in a solution; further, it was found that this solution, provided oxygen be present, is a solvent for gold. — J. C. Wells says that the figures obtained in the laboratory by Schneider for cyanide lost are much higher than the loss he (Wells) experienced in making large-scale tests on tailings. It amounted to only 0.44 and 0.4 pound per ton of ore, and of the 0.4 pound 0.24 pound was accounted for in the tailings, leaving 0.16 pound for the action of ore, air, and carbonic acid, while Schneider's experimental data called for an almost complete decomposition of the cyanide.

The Chemistry of the Cyanide Process — Is Zinc Potassium Cyanide a Solvent for Gold? By J. C. WELLS. *Eng. Mining J.*, **60**, 584. — The experiments made give an affirmative answer, but this solubility is of little or no importance in practical work, where there is always an excess of potassium cyanide, which is a much stronger solvent. The experiments show further that zinc potassium cyanide is not decomposed by alkali into potassium cyanide and potassium zincate. (*See this Quart.*, **8**, 333.) Finally the test with silver nitrate in the presence of caustic potash gives the total amount of cyanogen in solution, and not only the cyanide available as solvent for gold.

The Assay of Platinum. By E. H. MILLER. *School Mines Quart.*, **17**, 26–38. — The paper reviews the methods of Berzelius, Gibbs, Deville and Debray, Perry and Matthey, and gives the results obtained in trying to find a method for determining for commercial purposes the platinum contents of ores. The most satisfactory results obtained with pure platinum were those from a modification of Perry's method to scorify the ore with granulated lead,

treat the lead button with nitric acid (1.05 sp. gr.), oxidize the residue by heating, and remove the soluble oxide by treating with nitric acid (1.10 sp. gr.) for ten minutes at just below boiling point. The results accounted for 99.70, 99.72, and 99.71 per cent. of the platinum. With alloys the method must be extended to remove gold and platinum by warming the weighed residue from treatment with nitric acid (1.10 sp. gr.) with dilute (1 : 5) nitrohydrochloric acid, filtering off gold and platinum, igniting the residue and weighing it, evaporating the filtrate just to dryness, taking up with little hydrochloric acid, precipitating the gold with oxalic acid, filtering, cupelling, and weighing the gold, the difference giving the platinum. Iridium can be determined by treating the residue from the gold-platinum filtration with strong nitrohydrochloric acid, when iridium will go into solution, leaving iridosmium as insoluble residue.

The Manufacture of Bessemer Ferro-Silicon at Ashland, Ky. By J. C. Mathewson. *Eng. Mining J.*, **60**, 319. — The ferro-silicon used in this country has always been imported. This paper records the first successful attempt at making it here. The highest percentage of silicon obtained was 13.07 per cent.; the phosphorus, which in the ordinary high-silicon iron of Ashland lies between 1.0 and 1.4 per cent., sank to 0.1105 per cent.; the sulphur was higher than expected, viz., 0.051 and 0.054 per cent.

The Basic Blow. By F. E. Thompson. *Iron Age*, **56**, 1260–1262, 1318–1320. — The paper is a full discussion of the chemical and physical phenomena in blowing phosphoric pig in a basic converter. Many valuable analyses, accompanied by physical and technical data taken from the author's practical experience, give weight to the statements in the paper.

Apparatus.

A. H. Gill, Abstracter.

A Convenient Form of Universal Hand Clamp. By P. T. Austen and W. A. Horton. *J. Am. Chem. Soc.*, **17**, 611–612. — The device forms a convenient holder, capable of holding a needle, or a tube an inch and a half in diameter, allowing a grasp which corresponds to the weight of the object held, and not tiring the hand. It may be obtained through Richards & Company, New York.

Notes on Convenient Forms of Laboratory Apparatus. By D. A. Kreider. *Am. J. Sci.*, **50**, 132–134. — Hot filters, a valve for a mercury pump, and a force pump are described, for the details of which reference must be made to the original article.

A Convenient Still for the Laboratory. By Charles E. Wait. — *J. Am. Chem. Soc.*, **17**, 917–919. — The still has a capacity of seven gallons, and is arranged to be run with gas, furnishing twenty-six gallons per day; or with steam at 5 pounds, furnishing 112 gallons distilled water per day. It is connected with a water oven, which is so arranged as to serve partly as a condenser, and may or may not be used, as desired. It has also an automatic feed. A cut accompanies the article.

Index to the Review of American Chemical Research.

1895.

Abbot, C. G. (See Noyes, A. A.)
Adams, F. D. The Laurentian. 414.
——— Geology of Central Ontario. 210, 414.
Adams, R. C. Phosphate's Future. 327.
Anderson, N. Precipitation of Precious Metals from Cyanide Solutions by Zinc. 333.
Andresen, M. Composition of Commercial Sodium Sulphite. 322.
Andrews, L. Analysis of Alloys of Lead, Tin, Antimony, and Arsenic. 406.
Andrews, W. H. (See Campbell, E. D.)
Andrews, W. W. A Self-Regulating Gas Generator. 199.
Atkinson, E. A., and E. F. Smith. Separation of Iron from Beryllium. 317.
Atwater, W. O. Investigations on the Chemistry and Economy of Food. 326.
Auchy, G. Volumetric Estimation of Manganese. 409.
Austen, P. T., and W. H. Broadhurst. Absorbent Blocks. 199.
——— and W. A. Horton. A Universal Hand Clamp. 439.
Austin, L. S. Separation and Treatment of Lead Matte. 333.

Bachman, I. A. Chemical Brick for Glover Towers, 203.
——— Methods of Water Analysis. 108.
Bailey, E. H. S., and E. C. Franklin. Chemical Examination of the Kansas River. 327.
Balliet, L. Manufacture of Paving Brick. 321.
Baltwood, B. B. (See Wells, H. L.)
Bancroft, W. D. Ternary Mixtures. 306.
——— Chemical Potential of the Metals. 396.
Barlow, A. E. Some Dikes Containing Huronite. 208.
Bartlett, E. J., and W. H. Merrill. Cupric Hydride. 97.
Barton, G. E. Arsenic in Glycerol. 429.
——— Examination of Glycerol. 105.
Baskerville, C. Reactions between Copper and Sulphuric Acid. 401.
——— (See Venable, F. P.)
Bayley, W. S. Basic Massive Rocks of the Lake Superior Region. 114.
Beach, I. E. (See Evans, T.)
Beadle, C. (See Cross, C. F.)
Beeson, J. L. An Apparatus for Estimating the Water-Holding Power of Soils. 338.
Bell, J. C. Why Rubber Tires Deteriorate. 106.
Bell, R. Honeycombed Limestone in Lake Huron. 116.
de Benneville, J. S. Carbides of Iron with Chromium. 400.
Bergami, F. Citrate Method of Phosphoric Acid Determination. 318.
Berkey, C. P. Notes on Minnesota Minerals. 209.
Bevan, E. J. (See Cross, C. F.)
Bigelow, W. D. Coloring Matter in the California Red Wines. 109.
Birchall, F. W. Deterioration of India Rubber and its Causes. 431.
Blair, A. A., and J. E. Whitfield. Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reductor. 398.
Blasdale, W. C. Characteristics of Some California Oils. 432.
Blomen, J. E. Manufacture of Nitroglycerol. 105.
Boltwood, B. B. (See Wells, H. L.)
Bomen, J. E. Manufacture of Soluble Nitrocellulose. 203.
Boyer, C. S. Accuracy of the Dyeing Test. 203.
Bredel, F. Manufacture of Carbide of Calcium by Electrolysis. 201.
Breed, M. B. (See Keiser, E. H.)
Briggs, L. J. (See Guthe, K. E.)
Broadhurst, W. H. (See Austen, P. T.)
Brown, L. (See Meadows, T. C.)
Browne, D. H. Segregation in Ores and Mattes. 333, 417.
Bucherer, A. H. Theory of Electrolysis. 94.

Cady, H. P. (See Leighton, V. P.)
Cameron, F. K. (See Orndorff, W. R.)
Camp, J. M. Steel Analysis. 409.
Campbell, E. D. Oxidation of Gases with Palladinized Copper Oxide. 424.

Campbell, E. D., and W. H. Andrews. Separation of Nickel and Iron. 190.
——— ——— Nickel in Nickel Steel. 182.
Campbell, J. Hayes-. (See Cushman, A. S.)
de Chalmot, G. Oxidation of Complex Carbohydrates. 427.
——— Silicides of Iron. 401.
Chanute, O. Hydrogen Gas Apparatus. 119.
Church, J. A. Manganese Slags. 331.
Clark, E. Determination of Chromium in Chrome Ore. 186.
Clarke, F. W. Atomic Weights Published during 1894. 92.
——— Constitution of Silicates. 411.
Clarke, T. (See Venable, F. P.)
Clemons, C. F. (See Gooch, F. A.)
Coates, C. E., Jr. (See Remsen, I.)
Colburn, L. C. (See Slosson, E. E.)
Craver, W. A. (See Noyes, W. A.)
Cremer, F. Determination of Tungsten. 319.
Crocker, F. B. Theory of Electro-Metallurgy. 113.
Cross, C. F., E. J. Bevan, and C. Beadle. The Furfurol-Yielding Constituents of Plants. 199.
Cross, W. Laccolite Mountain Groups. 416.
Curtis, R. S. Experiments with Acetylacetone and Acetacetic Ether. 197.
Cushman, A. S. Separation of Copper and Cadmium. 190.
——— and J. Hayes-Campbell. Determination of Lead. 407.

Dains, F. B. Action of Acid Chlorides on Isobutylphenol Methyl Ether. 101.
——— and I. R. Rothrock. Bromine Derivatives of Isobutylphenol. 101.
Dale, T. N. (See Pumpelly, R.)
Day, W. C. Utah Gilsonite. 321.
Demond, C. D. (See H. O. Hofman.)
Derby, O. A. Constituents of the Cañon Diablo Meteorite. 114.
Desi, E. D. (See Smith, E. F.)
Doherty, H. L. Carbide of Calcium. 201.
Doremus, C. A. Combined Antimonial and Arsenical Poisoning. 330.
Dorrance, J. T. (See Noyes, A. A.)
Dorset, M. (See de Scweinitz, E. A.)
DuBois, H. W. (See Mixer, C. T.)
Dudley, C. B., and F. N. Pease. Determination of Ammonia in Ammonium Chloride. 189.
——— ——— Determination of Chloride in Ammonium Chloride. 189.
——— ——— Determination of Flashing and Burning Points of Combustible Liquids. 202.
——— ——— Determination of Specific Gravity of Oils. 411.
——— ——— Determination of Tar and Tar-Acids in Wood Preservative. 322.
——— ——— Determination of Cold Test and Chilling Point of Oils. 203.
Dudley, W. L. Heat of Vaporization of Gases. 397.
Dulin, R. S. Wet Assay for Copper. 187.
Dunnington, H. P. Gas Regulator. 338.

Eakle, A. S., and W. Muthman. Schneebergite. 415.
Edwards, W. F. Molecular and Atomic Refraction. 308.
Edwards, W. (See Knapp, M. A.)
Ehrenfeld, C. H. Behavior of Tungsten and Molybdenum and Their Trioxides. 191.
Elbers, A. D. Portland Cement and Blast Furnace Slag. 320.
——— (See Finnstone, F.)
Eldridge, G. H. Geological Reconnoissance in Northwest Wyoming. 420.
Ellis, R. M. (See Noyes, A. A.)
Evans, P. S. (See Gooch, F. A.)
Evans, T., and I. E. Beach. Determination of Rosin in Soap. 104.

Fairbanks, C. (See Gooch, F. A.)
Fairbanks, H. W. Analcite Diabase from California. 208.
Firmstone, F. Magnesia and Sulphur in Blast Furnace Cinder. 337.
Flory, B. S. Combustible in Smoke. 432.
Foote, W. M. New Alkali Mineral. 419.
Franklin, E. C. (See Bailey, E. H. S.)
Freer, P. C. Action of Chlorcarbonic Ester on Sodium Acetone. 99.
——— Action of Sodium on the Aconitic and Citric Esters. 100.
——— Tetrinic Acid. 428.
Friend, T. W. Recent Applications of the Nitrometer. 318.
Fuller, G. W. Sand Filtration of Water. 107.
Furman, H. V. F. Losses of Gold and Silver in the Fire Assay. 336.
——— Melting and Refining of Gold Bullion. 112.

Garrigues, W. E. Determination of Potash in Manures. 181.
Gibbs, W. Complex Inorganic Acids. 94.
Gifford, W. E. Chloride of Bromine as a Gold Solvent. 332.
Gill, A. H. Explosion Pipette. 338.
——— and S. P. Hunt. Determination of Methane and Hydrogen by Explosion. 411.
Gladding, S. T. Determination of Sulphur. 187.
Gomberg, M. Action of Some Inorganic Cyanides upon Chlorocaffeine. 196.
Gooch, F. A., and C. F. Clemons. Determination of Selenious Acid. 317.
——— and P. S. Evans. Reduction of Selenic Acid. 404.
——— and C. Fairbanks. Estimation of Halogens in Mixed Silver Salts. 317.
——— and I. K. Phelps. Determination of Carbon Dioxide. 318.
——— and W. G. Reynolds. Reduction of the Acids of Selenium. 318.

Gooch, F. A., and W. S. Scoville. Reduction of Selenic Acid. 404.
Gormly, S. J. Graphite Analysis. 417.
Government Reports. 420, 432, 434.
Griffith, A. B., and C. Platt. Composition of Pelagine. 423.
Grindley, H. S. (See Jackson, C. L.)
Grosvenor, W. M., Jr. New Solvents for Perchromic Acid. 97.
Guthe, K. E., and L. J. Briggs. Electrolytic Conductivity of Sulphuric Acid. 312.

Hall, C. W., and F. W. Sarderson. Magnesian Series of Northwestern States. 115.
Hall, W. T. (See Noyes, A. A.)
Handy, J. O. Barium Hydroxide Solution as a Carbonic Acid Absorbent. 185.
Hare, C. L. Qualitative Separation of the Iron Group. 315.
Harnly, H. J. Volcanic Dust. 207.
Harris, E. P. A New Generator. 338.
Harris, H. B. (See Smith, E. F.)
Hart, E. Condensation of Nitric Acid. 320.
——— Distillation of Nitric Acid. 320.
——— Glucinum Salts. 313.
Haworth, E. Crystalline Rocks of Missouri. 415.
Hayes, C. W. Bauxite Deposits. 413.
Heal, C. B., and H. R. Proctor. Analysis of Used Liquors in Chrome Tannage. 204.
Heath, G. L. Estimation of Sulphur in Refined Copper. 404.
Hering, R. Water Purification. 107.
Hibbard, P. L. Estimation of Starch. 109.
Hibbs, J. G. (See Smith, E. F.)
Higley, G. O. Action of Metals on Nitric Acid. 95.
Hill, E. A. Argon and Helium. 395.
——— Argon, Prout's Hypothesis, and the Periodic Law. 307.
Hillebrand, W. F. Calaverite from Cripple Creek, Colorado. 415.
——— Estimation of Titanium. 317.
Hills, R. C. The Costilla Meteorite. 117.
Hinds, J. I. D. A New Hydrogen Sulphide Generator. 199.
Hitchcock, F. R. M. Tungstates and Molybdates of Rare Earths. 313.
Hite, H. B. Determination of Molecular Weights by the Boiling-Point Method. 309.
Hobbs, W. H. Crystal Form of Borneol and Isoborneol. 198.
——— Mineralogical Notes. 414.
Hochstetter. (See Hofman.)
Hofman, H. O., and C. D. Demond. Refractoriness of Fire-Clays. 331.
Hofman and Hochstetter. Water Oven and Still. 119.
Horne, W. D. Decarbonization of Boneblack. 319.
Horton, H. E. Acidity of Glucose Syrup and Grape Sugar. 433.
——— Ash in Glucose Syrup and Grape Sugar. 433.
Horton, H. E. Manufacture of Syrup and Grape Sugar. 106.
——— Manufacture of Starch from Corn. 105.
Horton, W. A. (See Austen, B. T.)
Howe, H. M. Corrosion of Iron. 112.
——— Explanation of Kernel Roasting. 111.
——— (See Knapp, M. A.)
Howell, E. E. Two New Meteorites. 415.
Humphreys, W. J., and J. F. Mohler. Surface Tension of Water. 94.
Hunt, S. P. (See Gill, A. H.)
Hurlburt, E. B. (See Wells, H. L.)
Hyde, F. S. Identification of Acetanilide, Phenacetine, Quinine Sulphate, etc. 423.

Iddings, J. P. Absarokite-Shoshonite-Banakite Series. 420.
Iles, M. W. Temperature of Gases from Lead Furnaces. 436.
——— Temperature of Lead Slags. 436.

Jackson, C. L., and H. S. Grindley. Action of Sodic Alcoholates on Chloranil. 427.
Jewett, F. F. Washing Precipitates. 199.
Jones, H. C. Atomic Weight of Yttrium. 92.
——— Determination of Formic Acid. 317.
Joüet, C. H. Cretaceous Clays from Long Island. 117.

Kahlenberg, L. (See Hobbs, W. H.)
Kastle, J. H., and B. C. Keiser. Determination of Affinities of Acids. 306.
——— ——— Diazobenzeneaniline Chloride. 100.
——— New Reagent for Bromine and Iodine. 421.
——— and P. Murrill. Saponification of the Sulphonic Ethers. 194.
Kebler, L. F. Estimation of Vegetable Alkaloids. Study of Indicators. 405.
Keiser, B. C. (See Kastle, J. H.)
Keiser, E. H., and M. B. Breed. Action of Magnesium upon Alcohol Vapors. 426.
Keith, A. Geology of the Catoctin Belt. 417.
Kellar, E. Magnetic Oxide of Iron in Copper Mattes. 410, 437.
Keller, H. F., and P. Maas. Determination of Sulphur. 319.
Kennedy, W. Iron Ores of East Texas. 413.
Kerr, G. K. Tannin Determination. 321.
Kidwell, E. Stamp Sand in Cement Mortar. 106.
Kiefer, H. E. (See Shaber, W. B.)
Kilgore, B. W. Estimation of Phosphoric Acid. 408.
——— Determination of Phosphoric Acid. 409.
Knapp, M. A., G. McM. Ross, etc. Explanation of Kernel Roasting. 436.
Kohler, E. P. (See Remsen, I.)
Kortright, F. L. Effect of Hydrolysis upon Reaction Velocities. 90.

Kraemer, H. Chinquapin. 435.
Kreider, D. A. Laboratory Apparatus. 439.
——— Preparation of Perchloric Acid and Determination of Potassium. 190.
Kremers, E. Limonite and its Derivatives. 423.
——— (See Mead, J. L.)
Krug, W. H. Determination of Tannin. 430.

Landis, E. K. Calculation in Indirect Analysis. 188.
Lang, H. Matte Smelting. 113.
Langguth, W. Gold Sulphides. 334.
Laur, F. The Bauxites. 412.
Lea, M. C. Color Relations of Atoms, Ions, and Molecules. 307.
Lee, B. Water Supply. 107.
Leeds, A. R. Acetic Acid in Vinegar. 325.
Leighton, V. L., and H. P. Cady. Analysis of Counterfeit Gold Dust. 98.
——— ——— Solubility of Platinum in Hydrochloric Acid. 99.
Lengfeld, F., and J. Stieglitz. Imido-Ethers of Carbonic Acid. 100.
Lenher, V. Sulphiodide of Lead. 312.
Leonard, S. R., and J. H. Schnepel. Aluminum Alloys. 322.
Lewis, C. H. Reaction of Sodium Hyposulphite on Mercurous Chloride. 315.
Lichty, D. M. Rate and Limit of Esterification. 99.
Lindgren, W. Gold-Silver Veins of Ophir, California. 416.
Linebarger, C. E. Experiments in the Anthracene Series. 198.
——— Combination of Sulphur with Iodine. 96.
——— Formation of Layers in Mixtures of Acetic Acid and Benzene. 396.
——— Reaction between Zinc Sulphate and Potassium Hydroxide. 191.
——— Solubility of Salts in Organic Liquids. 93.
——— Relations between Temperature, Pressure, and Heat of Vaporization. 311.
——— Vapor-Tensions of Mixtures of Volatile Liquids. 310.
Linton, R. Study of Glass. 205.
Liversidge, A. Origin of Gold Nuggets. 118.
Lloyd, J. M. Detection of Starch. 435.
Long, J. H. Precipitation of Antimony. 97.
Lotz, D. (See Stone, W. E.)
Louis, H. Allotropism of Gold. 336.
Love, E. G. Acetylene as an Enricher. 201.
Low, A. H. Iodide Assay for Copper. 409.
Lunge, G. Estimation of Sulphur in Pyrites. 184, 404.
Luquer, L. McI. Sodalite. 206.
Lychenheim, J. Phosphorus in Coal and Coke. 319.

Maas, P. (See Keller, H. F.)
Mabery, C. F. American Sulphur Petroleums. 323.
Mabery, C. F. Atmosphere of a Large City. 108.
MacGregory, A. C. Electric Conductivity of Salt Solutions. 93.
Mathews, F. M. (See Smith, E. F.)
Mathewson, J. C. Manufacture of Bessemer Ferro Silicon. 439.
Matos, L. J. Bleaching of Textile Colors by Electricity. 322.
Matthew, W. D. Effusive and Dyke Rocks near St. John, New Brunswick. 420.
McCay, L. W. Sulphoxyantimonates. 402.
McElroy, K. P. Estimation of Iron and Alumina in Phosphates. 185.
McKenna, A. G. Improvement in the Zinc Reductor. 409.
——— Barium Hydrate as an Absorbent. 189.
McPherson, W. (See Weber, H. A.)
McTaggert, J. R. (See Noyes, W. A.)
Mead, D. W. Water Supply. 107.
Mead, J. L., and E. Kremers. From Pinine to Carvacrol. 422.
Meadows, T. C., and L. Brown. Phosphates of Tennessee. 414.
Merril, G. P. Disintegration of Granite Rocks. 117.
Merrill, W. H. (See Bartlett, E. G.)
Meyer, F. L. (See Smith, E. F.)
Miller, A. S. Behavior of Ammonia toward Ferric and Ferrous Chlorides. 314.
Miller, E. H. Assay of Platinum. 438.
Mitchell, W. L. (See Wells, H. L.)
Mixer, C. T., and H. W. DuBois. Iron in Iron Ores. 187.
Mixter, W. G. Azo and Azimido Compounds. 197.
Mohler, J. F. (See Humphreys, W. J.)
Monroe, C. E. Inspection of Cotton for Guncotton Manufacture. 431.
Morley, E. W. Atomic Weight of Oxygen. 305.
Morse, F. W., and A. H. Wood. Maple Sap. 325.
Murrill, P. (See Kastle, J. H.)
Muthman, W. (See Eakle, A. S.)

Neiman, H. S. Color and Composition in the Tetrazo Group. 107.
Nickum, J. W. Anatolian Licorice Root. 435.
Norris, R. S. Action of Light on Lead Bromide. 97.
Norton, T. H. Methods of Preventing Conflagration. 200.
Noyes, A. A., and C. G. Abbot. Dissociation from Solubility and Conductivity Experiments. 308.
——— and J. T. Dorrance. Electrolytic Reduction of Paranitro Compounds. 424.
——— and R. M. Ellis. Synthesis of Diphenylbiphenyl Benzerythrene. 422.
——— and W. T. Hall. Rate of Hydrolysis of Salicine with Acids. 396.
——— and W. H. Watkins. Trimethylene Glycol as a By-Product. 427.
Noyes, W. A. Camphoric Acid. 196.

Noyes, W. A., J. R. McTaggart, and H. W. Craver. Determination of Heating Effects of Coals. 433.
——— and J. S. Royse. Phosphorus in Steel and Cast Iron. 183.

Oenslager, G. (See Richards, T. W.)
Orndorff, W. R., and F. K. Cameron. Apparatus for Determination of Molecular Weights. 309.
——— ——— Paranthracene. 425.
Osborne, J. B. Proteids of the Rye Kernel. 328.
Osborne, T. B. Chemical Nature of Diastase. 329.
——— Proteids of Barley. 328.

Packard, R. L. Occurrence of Copper in Western Idaho. 418.
Palmer, A. D., Jr. Wave Length of the D_3 Helium Line. 397.
Palmer, C. S., and W. B. Stoddard. Dyke on the Columbian Vein, Ward District, Colorado. 418, 420.
Palmer, C. Chromates of the Rare Earths. 193.
Parker, D. T. (See Seamon, W. H.)
Parr, S. W. Proximate Analysis of Coal. 411.
Peabody, W. L. Tannin of Cloves. 43.
Peale, A. C. Mineral Waters of the United States. 416.
Pearce, R. Occurrence of Tellurium with Gold. 418.
Pease, F. N. (See Dudley, C. B.)
Peckham, S. F. The Asphalt Question. 105.
Pemberton, H., Jr. Determination of Phosphoric Acid. 184.
Penfield, S. L. Separation of Minerals of High Specific Gravity. 397.
——— and J. H. Pratt. Optical Properties of Lithiophilite and Triphylite. 418.
Pfordte, O. F. The Cerro de Pasco Mining Industry. 334.
Phelps, I. K. (See Gooch, F. A.)
Phillips, F. C. Determination of Sulphur in White Cast Iron. 407.
——— Occurrence of Hydrogen and Methane in the Atmosphere. 399.
Phillips, W. B. Notes on Magnetite. 414.
Pirsson, L. V. (See Weed, W. H.)
Platt, C. (See Griffith.)
Pratt, J. H. (See Penfield, S. L.)
——— Double Halides of the Alkali Metals with Thallium. 194.
Prescott, A. B., and P. F. Trowbridge. Periodides of Pyridine. 424.
Proctor, H. R. (See Heal, C. B.)
——— Tannin Determination. 106.
Prosser, C. S. Upper Paleozoic Rocks of Central Kansas. 420.
Pumpelly, R., J. E. Wolff, and T. Nelson Dale. Geology of the Green Mountains in Massachusetts. 416.
Pupin, M. I. Automatic Mercury Vacuum Pump. 200.

Quinan, W. R. Argon. 310.

Ramsay, W. (See Lord Rayleigh.)
Ransome, F. L. Lawsonite. 208.
Rayleigh, Lord, and W. Ramsay. Argon. 192.
Reed, C. J. Electrolytic Phenomenon. 397.
——— Prediction of Existence of Argon. 307.
Remsen, I., C. E. Coates, E. P. Kohler, and A. P. Saunders. Chlorides of *o*-Sulphobenzoic Acid. 194.
Reynolds, W. G. (See Gooch, F. A.)
Richards, J. W. Recent Advances in Electro-Chemistry. 322.
——— Reduction of Alumina. 432.
——— Aluminum Alloys. 113.
Richards, T. W. Cupriammonium Double Salts. 96, 193.
——— Composition of Athenian Pottery. 320.
Ridenour, W. E. Derivatives of Chimaphilin. 434.
——— Analysis of Commercial Cacaos. 436.
Ries, H. Clay Industries of New York. 210.
Robertson, J. D. (See Winslow, A.)
de Roode, R. Determination of Potash in Fertilizers. 181, 182.
——— Potash in Kainite. 182.
——— Preparation of Ammonium Citrate Solution. 181.
Rosell, C. A. O. The Ferrates. 399.
Ross, G. McM. (See Knapp, M. A.)
Rothrock, I. R. (See Dains, F. B.)
Rothwell, J. E. Chlorination Barrel. 437.
——— Precipitation of Gold. 437.
Rowland, H. A. Solar Spectrum Wave Lengths. 94, 312, 397.
Royse, J. S. (See Noyes, W. A.)
Runyan, E. G., and H. W. Wiley. Determination of Phosphoric Acid. 315.
Russel, C. P. Naphthalene. 433.
Russell, T. H. Amalgamation and the Russell Process. 112.

Sacio, V. P. y. Tina-Amalgamation. 334.
Sadtler, S. P. Asphalts and Bitumens. 321.
——— Technical Analysis of Asphalt. 410.
Sarderson, F. W. (See Hall, C. W.)
Sauer, E. Some New Laboratory Apparatus. 199.
Saunders, A. P. (See Remsen, I.)
Sayre, L. E. Taxaracum Root and Taxaracin. 435.
Schlundt, H., and R. B. Warder. Chemical Kinetics of Oxydation. 395.
Schmitz-Dumont, W. Examination of Fats. 413.
Schneider, A. Cyanide Process. 112, 410, 438.
Schneider, E. A. Cyaniding or Chlorination. 332.
Schnepel, J. H. (See Leonard, S. R.)
Schniewind. Gas from Coke Ovens. 202.
Scoville. (See Gooch, F. A.)
de Scweinitz, E. A., and M. Dorset. Composition of Tuberculosis and Glanders Bacilli. 329.

Seamon, W. H., and D. T. Parker. Alchemist's Symbols. 330.
——— ——— Losses in Gold and Silver in Cupelling. 336.
——— History of Zinc. 330.
Seldner, R. Glutarimide. 427.
Sherman, H. C. Determination of Nitrogen in Fertilizers. 316, 327.
Shimer, P. H. Graphite in Pig Iron. 406.
——— Determination of Zinc. 186.
Shiver, F. S. Standardization of Sulphuric Acid. 187.
Shober, W. B., and H. E. Kiefer. Action of Alcohols with *m*-Diazobenzenesulphonic Acid. 198.
Shutt, F. T. Well Waters of Our Farm Homesteads. 107.
——— Phosphoric Acid in Agriculture. 327.
Slocum, F. L. Acetylene. 201.
Slosson, E. E., and L. C. Colburn. Heating Power of Wyoming Coal and Oil. 202.
Smart, C. Pollution of Water Supplies. 107.
Smith, E. F., and E. D. Desi. Atomic Weight of Tungsten. 307.
——— and H. B. Harris. Electrolytic Determination of Ruthenium. 316.
——— Action of Phosphorus Pentachloride upon Zirconium and Thorium Dioxides. 313.
——— and J. G. Hibbs. Action of Hydrochloric Acid Gas upon Salts of Elements of Group V. 313.
——— and T. M. Mathews. Uranium Oxynitride and Uranium Dioxide. 314.
——— and F. L. Meyer. Action of Gaseous Haloid Acids upon Salts of Elements of Group V. 314.
——— and D. L. Wallace. Electrolytic Separations. 316.
——— (See Atkinson, E. A.)
Smith, J. B. Canadian Phosphate and Fertilizers. 327.
Smyth, C. H., Jr. Limestones of the Adirondack Region. 116.
Snyder, H. Action of Acids upon Soils. 110.
Spencer, H. G. Composition of Lead and Zinc Ores. 117.
——— Composition of Cleaned Ores of Southwest Missouri. 417.
Spenzer, J. G. β-Bromvalerianic Acid. 103.
——— Behavior of Unsaturated Acids with Caustic Soda Solution. 102.
Squibb, E. R. Manufacture of Acetone. 103.
Stetefeldt, C. A. Commercial Assay for Silver. 335.
——— Marsac Refinery. 332.
——— The Stetefeldt Furnace. 331.
Stieglitz, J. (See Lengfeld, F.)
Stillman, J. M., and M. B. Yoder. Combination of Anhydrous Ammonia and Aluminium Chloride. 402.
Stoddard, W. B. (See Palmer, C. S.)
Stokes, H. N. Chloronitrides of Phosphorus. 192.
Stone, G. E. Determination of Zinc. 188.
Stone, W. E. Action of Ammonia upon Dextrose. 102.
Stone, W. E. Carbohydrates of the Gum of Acacia Decurrens. 111.
——— and D. Lotz. The Sugar of the Agave Americana. 199.
Struthers, J. Slags from Lead Furnaces. 331.
Suckert, J. J. (See Willson, T. L.)
Sulman, H. L. Cyanogen Bromide and Potassium Cyanide for Dissolving. 112.
Sulman. (See Schneider.)

Teed, F. A. Cyanogen Bromide for Dissolving Gold. 332.
Tennille, G. F. Phosphomolybdic Acid Test in Lard Analysis. 109.
Thomas, W. S. Determination of Manganese. 186.
Thompson, F. E. Basic Bessemer Process. 335.
——— The Basic Blow. 439.
Thornton, T. R. Tannin of Cinnamonum Cassia. 435.
Torrey, H. G. Cupels. 111.
Trevor, J. E. Law of Mass Action. 305.
Trowbridge, P. F. (See Prescott, A. B.)
Trubek, M. Estimation of Extraction in Sugar Houses. 433.
True, A. C. Agricultural Experiment Stations. 327.
Turner, H. W. Rocks of Sierra Nevada. 417.
——— Igneous Rocks of the Sierra Nevada. 206.

Venable, F. P. Arrangement of the Elements. 92, 395.
——— Chlorides of Zirconium. 400.
——— and C. Baskerville. Zirconium Sulphite. 192.
——— and T. Clarke. Calcium Carbide. 189.
Volckening, G. J. (See Luquer, L.)

Wait, C. E. A Still for the Laboratory. 439.
Waldo, L. Aluminum Bronze. 335.
Walker, M. S. Preparation of Potassium Ferricyanide. 96.
Walker, P. H. Preparation of Barium and Calcium Ferrocyanides. 401.
Walker, T. L. Diabase Dykes. 118.
Wallace, D. L. (See Smith, E. F.)
Ward, H. A. The Plymouth Meteorite. 114.
Warder, R. B. (See Schlundt, H.)
Waring, G. Purification of Sewage. 326.
Warwick, A. W. Solution of Gold in Cyanide. 332.
Washington, H. S. Petrographical Sketch of Ægina and Methana. 115.
Watkins, W. H. (See Noyes, A. A.)
Weber, H. A. and W. McPherson. Action of Acids on Sucrose. 324.
——— ——— Determination of Cane Sugar in Commercial Glucose. 323.
Weed, W. H., and L. V. Pirsson. Igneous Rocks of Yogo Peak, Montana. 418.
Weeks, J. D. Coal Fields of West Virginia. 417.
Wells, H. L. Compounds Containing Lead and Extra Iodine. 314.

Wells, H. L., and B. B. Boltwood. Double Salts of Cæsium Chloride with Chromium and Uranyl Chlorides. 315.
——— and E. B. Hurlburt. Ammonium Cuprous Double Halogen Salts. 403.
——— and W. E. Mitchell. Determination of Titanic Acid and Iron in Ores. 407.
Wells, J. C. Cyanide Process. 438.
Wells, J. S. C. Bromo-Cyanide Process. 332.
——— Cyanide *vs.* Cyanide Plus Cyanogen Bromide. 333.
Wesson, D. Examination of Lard for Impurities. 325.
Wheeler, H. L. Action of Benzimidomethyl Ether on Aromatic Ortho-Compounds. 196.
——— Action of Bromine on *m*-Nitraniline. 423.
——— Halogen Addition-Products of the Anilides. 421.
White, J., Jr. Investigations on the Sulphonthaleïns. 425.
Whitefield, J. E. (See Blair, A. A.)
Whitehead, C. Estimation of Tellurium. 185.
——— Tellurium. 400.
Whitridge, A. H. (See Richards, T. W.)
Wiechmann, F. G. Basswood Oil. 198.
——— Crystalline Compounds of Sucrose, Dextrose, and Levulose. 427.
——— Sugar-Ash Analysis. 189.
Wigglesworth, H. Canada, a Natural Manufacturing Center for Fertilizers. 327.
Wiley, H. W. Analysis of Cereals. 326.
——— Synthetic Food of the Future. 109.
——— (See Runyan.)
Williams, C. B. Estimation of Phosphoric Acid in Soils. 408.
——— Manufacture of White Lead. 430.
Willson, T. L., and J. J. Suckert. Carbides and Acetylene Commercially Considered. 323.
Wilson, T. Presence of Fluorine as a Test for Fossilization. 207.
Winslow, A. Lead and Zinc Deposits of Missouri. 209.
Winton, A. L. Determination of Potash as Potassium Platinichloride. 188.
Wolff, F. A., Jr. Effect of Magnetism on Chemical Action. 91.
Wolff, J. E. (See Pumpelly, R.)
Wood, A. H. (See Morse.)
Wood, M. P. Carbide of Calcium. 201.
Wyatt, F. Fixation of Atmospheric Nitrogen and the Manufacture of Cyanides and Ammonia. 320.
——— Purification of Boiler Feed Waters. 321.

Yoder, M. B. (See Stillmann, J. M.)

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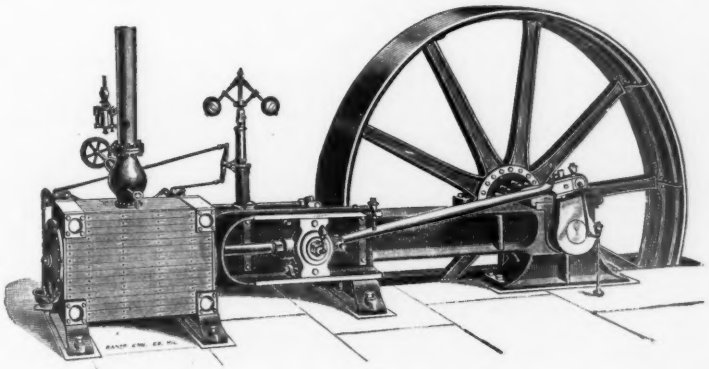

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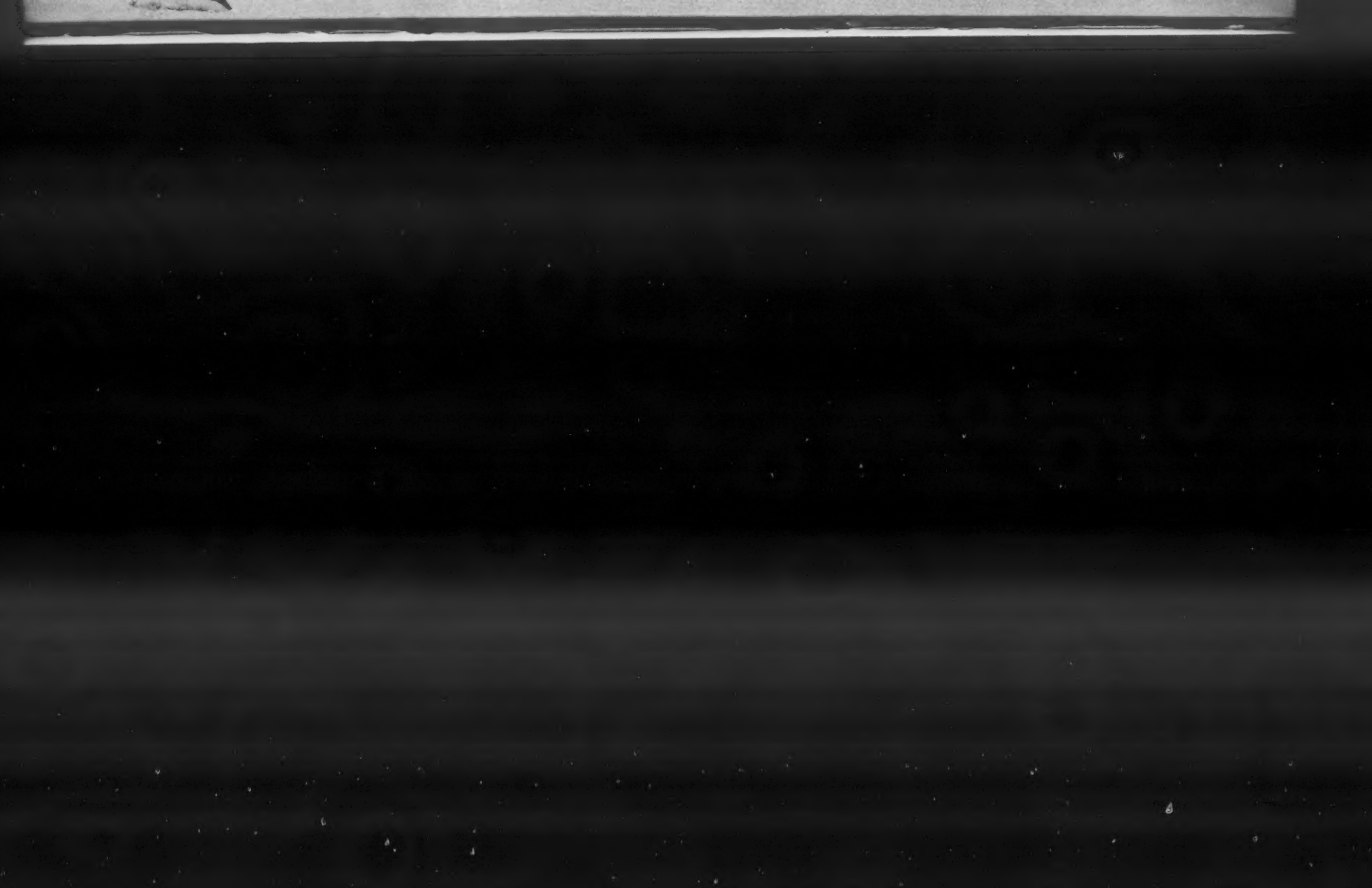

Vol. VIII. DECEMBER, 1895. No. 4.

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TECHNOLOGY QUARTERLY

AND PROCEEDINGS OF THE SOCIETY OF ARTS

CONTENTS

		PAGE
Proceedings of the Society of Arts		341
Calorimetry. Methods of Correction for Cooling	*Silas W. Holman*	344
Thermo-Electric Interpolation Formulæ	*Silas W. Holman*	353
Treatment of Roasted Gold Ores by Means of Bromine,	*Richard W. Lodge*	378
On Pure Yeast and Hansen's Method for its Cultivation,	*Simeon C. Keith, Jr.*	383
The Cyanide Process as Applied to the Concentrates from a Nova Scotia Gold Ore	*Richard W. Lodge*	389
Review of American Chemical Research		395
Index to the Review of American Chemical Research, 1895		440

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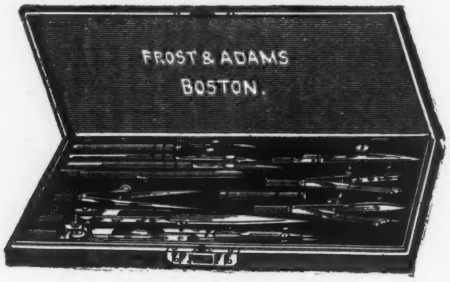

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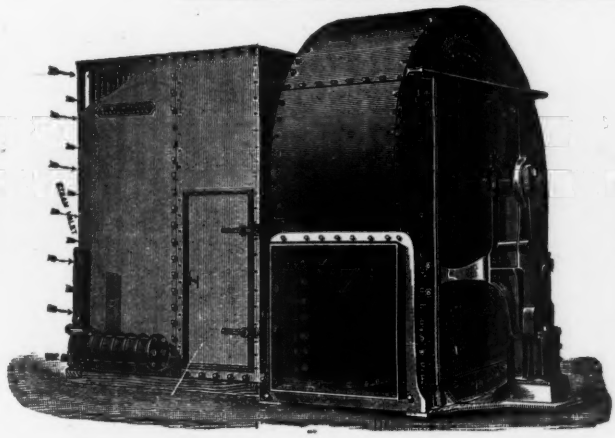

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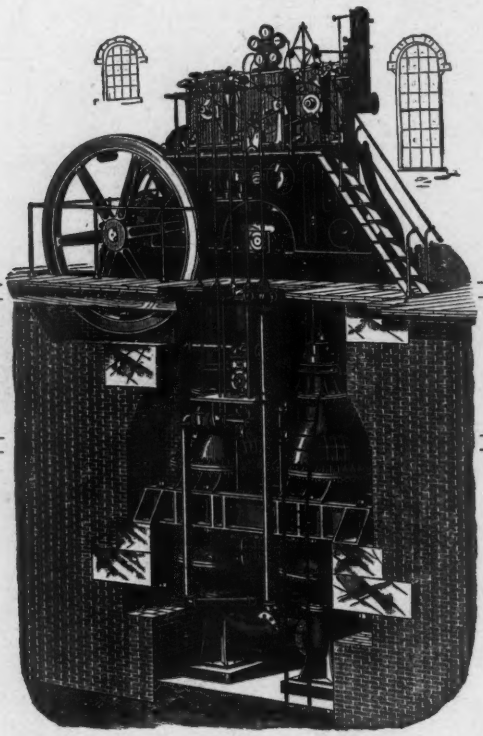

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